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Surrogate and Matrix Spike Recoveries in Chlorinated Samples Using Sodium Thiosulfate, Sodium Arsenite and L-Ascorbic Acid as Dechlorinating Agents

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Abstract: Chlorine reacts with various organics in environmental samples to produce undesirable artifacts. These artifacts can cause false positives to be reported, and other compounds actually present to be reported as not detected. The NPDES method (EPA Method 625) for base/neutral and acid compounds states that residual chlorine should be determined in the field. Effluents must be dechlorinated before acidification to prevent the chlorination of compounds present in the effluent. The study examined the suitability of three dechlorinating agents: sodium thiosulfate, L-ascorbic acid and sodium arsenite. The three dechlorinating reagents were also tested using the separatory funnel technique. The authors are currently using continuous extraction as the routine method of extraction for water samples. This method has been found to generally produce higher recoveries of all compounds when compared to separatory funnel extraction. The higher recoveries are due to the fact that the extraction solvent is constantly being re-distilled. This essentially results in numerous, repeated extractions using fresh solvent for each extraction.

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SURROGATE AND MATRIX SPIKE RECOVERIES IN CHLORINATED SAMPLES USING SODIUM THIOSULFATE, SODIUM ARSENITE AND L-ASCORBIC ACID AS DECHLORINATING AGENTS

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SURROGATE AND MATRIX SPIKE RECOVERIES IN CHLORINATED SAMPLES USING SODIUM THIOSULFATE, SODIUM ARSENITE AND L-ASCORBIC ACID AS DECHLORINATING AGENTS*

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Method 625 (Base/Neutrals and Acids) (1) states that samples containing residual chlorine must be dechlorinated using 80 mg of sodium thiosulfate per liter of sample (Section 9.2) at the time of sampling. Field conditions are difficult to control and it is conceivable that excess amounts could be added. Analytical problems have been encountered using this reagent when excess thiosulfate has been added to samples. Sulfur crystal formation occurred in the Kuderna-Danish concentration process and caused frothing of the concentrate. This can easily cause the sample to go to dryness. Also, the elution of molecular sulfur caused severe chromatographic interferences. These problems were especially evident when the samples were extracted using continuous liquid/liquid extraction. The sulfur formation occurred under acid (pH<2) extraction conditions as a result of the decomposition/disproportionation of thiosulfate to sulfur and sulfite/sulfur dioxide (2).

Two alternate dechlorination agents were tested: L-ascorbic acid and sodium arsenite. Both were efficient at reducing the chlorine. Sodium arsenite treatment resulted in a clean chromatogram and no analytical problems. L-ascorbic acid treatment generated five chromatographic interference peaks when the extraction was performed with the continuous extractor. These were: 2-furancarboxylic acid; 3-furancarboxylic acid, methyl ester; 2-furancarboxaldehyde; 3,5-dihydroxy-2-methyl-4H-pyran-4-one; and one unidentified peak. These five compounds were tentatively identified using the EPA-NIH spectral library. The mass spectrum of 2-furancarboxylic acid contained a fragment with mass 45 amu and would be expected to elute near bis(2-chloroisopropyl)ether. The base peak of this priority pollutant is also 45 amu. This contaminant could cause a positive interference which should be resolvable by manual quantitation or by reducing the automated target search windows. No contaminating peaks were detected when samples were dechlorinated with L-ascorbic acid and extracted using separatory funnels.

Sodium arsenite is listed as extremely toxic to humans with an oral lethal dose of less than 5 mg/kg (3), and would be too dangerous for routine field use. L-ascorbic acid is

non-toxic and is more soluble in water than sodium arsenite. L-ascorbic acid has been recently recommended as a dechlorinating agent of choice for VOCs (EPA QA Newsletter, January, 1988) (4), and it would be convenient to use the same material to dechlorinate samples for extractable organics. However, low recoveries (about 30% of a 50 ug/L spike) of 2,4-dinitrotoluene were obtained when the extraction was carried out in the presence of excess L-ascorbic acid using Method 625 (continuous extraction).

*This work was first presented in the EPA Quality Assurance Newsletter, July 1988, Volume 10, Number 2.

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The mention of trade names or commercial products in this report is for illustrational purposes and does not constitute endorsement or recommendation by the U.S. Environmental Protection Agency.

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I. INTRODUCTION

Chlorine reacts with various organics in environmental samples to produce undesirable artifacts. These artifacts can cause false positives to be reported, and other compounds actually present to be reported as not detected. For example, phenol concentrations may decrease in chlorinated effluents, forming various mono- and poly- chlorinated phenols. When phenols are reacted with aqueous solutions of halogens, polyhalogenation of the phenolic ring occurs (5). On the other hand, monohalogenated compounds are the primary products formed if the reaction occurs in a non-polar solvent such as carbon tetrachloride or chloroform (5). Reactions in methylene chloride could be expected to produce a similar reaction.

The NPDES method (EPA Method 625) (1) for base/neutral and acid compounds states that residual chlorine should be determined in the field. Any residual chlorine present is to be removed using 80 mg of sodium thiosulfate per liter of sample. The EPA Newsletter of January 1988 contained a "Note on Preservation of Drinking Water Samples to be Analyzed for Volatile Organic Chemicals (VOCs) and 1445 Monitoring Compounds" (4). This note stated that effluents must be dechlorinated before acidification to prevent the chlorination of compounds present in the effluent. It was reported that when sodium thiosulfate was used as a dechlorinating agent for VOA analysis, SO_2 interfered with the early-eluting VOA gases. Ascorbic acid was recommended as a substitute. It did not produce any chromatographic interferences.

This study examined the suitability of three dechlorinating agents: sodium thiosulfate, L-ascorbic acid and sodium arsenite. In the initial series of experiments, EPA Method 625 (1) (<u>continuous extraction option</u>) was used for the analysis. One variation to the method was employed; base/neutral and acid extracts were combined before GC/MS analysis. A second series of experiments were also performed using acid/neutral extraction conditions (<u>continuous extraction</u>) followed by a basic extraction. <u>Base/neutral, acid</u> refers to an extraction scheme in which the sample pH is first adjusted to pH >11. This results in the extraction of basic and neutral compounds. Fresh solvent is then added, and the pH is adjusted to <2. Acidic compounds will be extracted in this fraction. <u>Acid/neutral, base</u> refers to an extraction scheme in which the sample pH is first adjusted to pH <2. This results in the extraction of acidic and neutral compounds. Fresh solvent is then added, and the pH is adjusted to >11. Basic compounds will be extracted in this fraction.

The effect of chlorination would be expected to be intensified under acid/neutral conditions, since chlorine

would be in the free reactive state (6). Under basic conditions, most of the chlorine would be present as hypochlorite ion (6).

$$Cl_2 + H_2O \underset{pH<4}{\overset{pH>4}{<==>}} HCl + HOCl$$

$$HOCl \underset{pH<9}{\overset{pH>9}{<==>}} H^+ + OCL^-$$

The three dechlorinating reagents were also tested using the separatory funnel technique. Excess amounts of each reagent were used to determine analytical problems, including chromatographic interferences. In a separate test, 160 mg of sodium thiosulfate was employed as a dechlorinating agent and tested for analytical problems.

The effect of L-ascorbic acid dechlorination was further tested using spikes of nitrobenzene, 2.4-dinitrotoluene and 2,6-dinitrotoluene. Extractions were performed by the continuous extraction method.

In a final series of experiments, sodium thiosulfate was tested using 20 and 80 mg levels of this reagent. Both levels were tested using continuous extraction. A separatory funnel analysis using 80 mg/L of sodium thiosulfate was also performed.

The authors are currently using continuous extraction as the routine method of extraction for water samples. This method has been found to generally produce higher recoveries of all compounds when compared to separatory funnel extraction (7). The higher recoveries are due to the fact that the extraction solvent is constantly being re-distilled. This essentially results in numerous, repeated extractions using fresh solvent for each extraction.

II. REAGENTS AND SUPPLIES

Brand names and catalog numbers are included for illustrational purposes only.

a. Chlorox, commercial brand, 5.25% sodium hypochlorite.
b. Hach DPD Kit, Model # CN-66, containing DPD reagent total chlorine reagent powder pillows part, #14076-99.
c. Sodium Hydroxide, J.T. Baker, pellet form, #3728-1. 6N NaOH prepared by adding 240 g of NaOH to a 1000 mL volumetric flask and diluting to volume.
d. Methylene chloride, B & J high purity solvent, product #300, contains cyclohexene preservative to inhibit HCl formation.
e. Sulfuric acid, Baker, Instra-Analyzed, #9673-03. 6N H_2SO_4 prepared by slowly adding 167 mLs of concentrated H_2SO_4 to 833 mLs of reagent water.
f. Multi-range pH paper strips, EM-Reagents ColorpHast pH indicator strips, pH 0-14.
g. Boiling Stones, Hengar Co., carborundum #12 granules, #133-B. Conditioned by muffling at 450°C for 3-4 hrs.
h. Sodium thiosulfate, Baker, anhydrous, granular, #1-3954.
i. Sodium arsenite, meta, Fisher, #S225.
j. L-Ascorbic acid, Fisher, #A-61.
k. Sodium sulfate, anhydrous, granular, Mallinckrodt, product #8024 . Muffled for 3-4 hours at 450°C. Stored in glass.
l. Glasswool, Pyrex brand, fiber glass, sliver 8 micron, Corning Glass Works. Muffled for 3-4 hours at 450°C.

III. STANDARD PREPARATION

A. SPIKING SOLUTION PREPARATION

The surrogate spike mix contained the following compounds (at a concentration of 500 ug/mL, except tribromophenol which was 1500 ug/mL): 2-fluorophenol; d_5-phenol; d_5-nitrobenzene; 2-fluoro-1,1'-biphenyl; 2,4,6-tribromophenol; and d_{14}-p-terphenyl. The following standards, obtained from the EPA Quality Assurance Materials Bank in RTP, N.C., were used in the preparation of the surrogate standard mix:

2,4,6-tribromophenol, #875-01-03, in methanol, 5000 ug/mL
d_{14}-p-terphenyl, #909-03-01, in tetrahydrofuran, 5000 ug/mL
Organics Surrogate Mix, #C088-01, in methylene chloride contained the following compounds, each present at a concentration of 5000 ug/mL:

2-fluorophenol
d_5-phenol
d_5-nitrobenzene
2-fluoro-1,1'-biphenyl
2,4,6-tribromophenol

The surrogate mix was prepared by pipetting 1 mL of #C088-01, 2 mLs of 2,4,6-tribromophenol and 1 mL of d_{14}-p-terphenyl into a 10 mL volumetric flask and diluting to volume with acetone.

The matrix spike solution for acidic compounds (in methanol) contained the following compounds at a concentration of 1000 ug/mL: phenol; 4-chloro-3-methylphenol; 4-nitrophenol; 2-chlorophenol and pentachlorophenol. The following standards, obtained from the EPA Quality Assurance Materials Bank in RTP, N.C., were used in the preparation of this mix:

Phenol, #63-01-06, in methanol, 5000 ug/mL
4-chloro-3-methylphenol, #20-02-02, in methanol, 5000 ug/mL
4-nitrophenol, #56-01-06, in methanol, 5000 ug/mL
2-chlorophenol, #22-03-03, in methanol, 5000 ug/mL
pentachlorophenol, #62-03-13, in methanol, 5000 ug/mL

The matrix spike solution for acidic compounds (hereafter referred to as acid matrix spike) was prepared by adding 2 mLs of each stock standard to a VOA vial. The standards diluted each other to a final concentration of 1000 ug/mL.

The matrix spike solution for basic and neutral compounds contained the following compounds (at a concentration of 500 ug/mL each, except for pyrene which was 100 ug/mL): 1,4-dichlorobenzene; n-nitroso-di-n-propylamine; 1,2,4-trichlorobenzene; acenaphthylene/acenaphthene; 2,4-dinitrotoluene; di-n-butyl phthalate and pyrene. The following standards, obtained from the EPA Quality Assurance Materials Bank in RTP, N.C., were used in the preparation of this mix:

1,4-dichlorobenzene, #25-02-03, in methanol, 5000 ug/mL
n-nitroso-di-n-propylamine, #61-03-02, in methanol,5000 ug/mL
1,2,4-trichlorobenzene, #07-01-08, in methanol, 5000 ug/mL
acenaphthylene, #75-01-04, in methanol, 5000 ug/mL
acenaphthene, #75-02-02, in methanol, 5000 ug/mL
2,4-dinitrotoluene, #33-02-03, in methanol, 5000 ug/mL
di-n-butyl phthalate, #66-01-07, in methanol, 5000 ug/mL
pyrene, #82-03-01, in methanol, 5000 ug/mL

The matrix spike for basic and neutral compounds (hereafter referred to as base/neutral matrix spike) was prepared by adding 1 mL of each standard to a 10 mL volumetric flask and diluting to volume with acetone.

B. INTERNAL STANDARDS

a. Supelpreme-HC Internal Standards Mix, 4000 ug/mL each in 1 mL methylene chloride:

d_{10}-acenaphthene	d_8-naphthalene
d_{12}-chrysene	d_{12}-perylene
d_4-1,4-dichlorobenzene	d_{10}-phenanthrene

All extracts were spiked with the internal standards mix just prior to GC/MS analysis.

C. NITROBENZENE AND 2,4-DINITROTOLUENE STANDARD

Prepared by pipetting 1 mL of each of the following into a 10 mL volumetric flask and diluting to volume with methanol.

a. Nitrobenzene, #54-01-08, in methanol, 5000 ug/mL
b. 2,4-dinitrotoluene, #33-02-03, in methanol, 5000 ug/mL

Both standards were obtained from the EPA Quality Assurance Materials Bank in RTP, North Carolina. The final concentration of the working standard was 500 ug/mL.

D. 2,6-DINITROTOLUENE STANDARD

Prepared by pipetting 1 mL of the following into a 10 mL volumetric flask and diluting to volume with acetone:

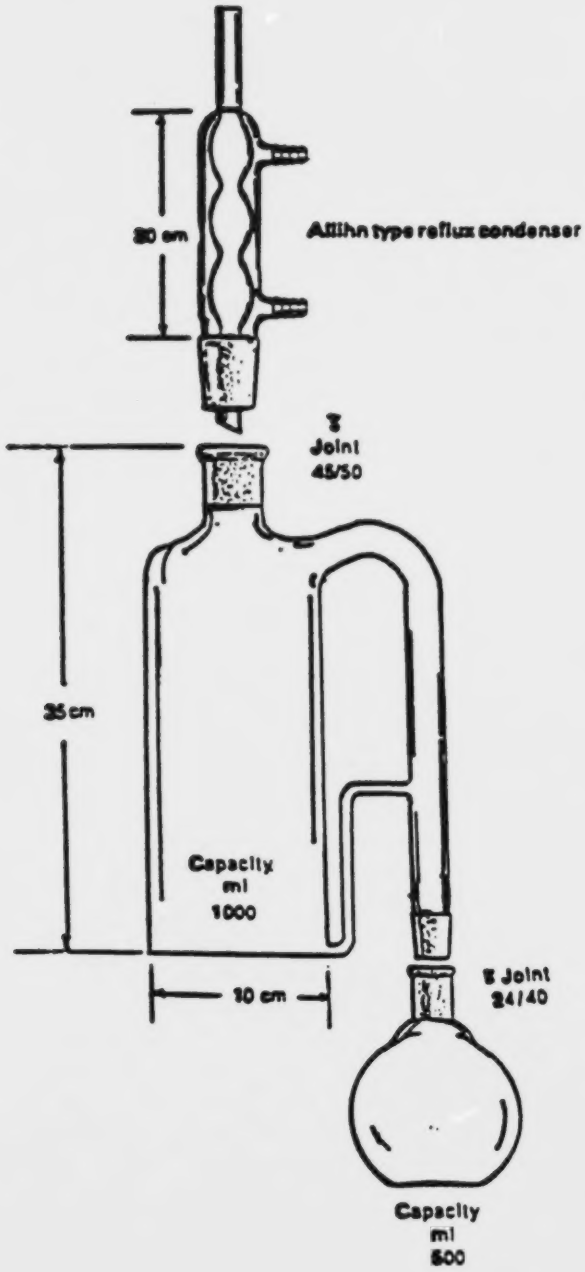
2,6-dinitrotoluene, #606-20-2, in methanol, 5000 ug/mL

This standard was obtained from the EPA Quality Assurance Materials Bank in RTP, North Carolina. The final concentration of the working standard was 500 ug/mL.

IV. APPARATUS AND MATERIALS

a. Muffle furnace, Blue M Power-O-Matic 80.
b. Muffle furnace, Blue M Touch Master, Model #CFD-20F-6.
c. Heating mantle, Glas-Col Apparatus Co., Cat. No. TM102.
d. Variable transformer, Staco Energy Products Co., type 3PN1010.
e. 500 mL boiling flask.
f. 1000 mL graduated cylinder.
g. Allihn condenser, 45/50 joint.
h. 3-ball Snyder columns, macro and micro.
i. 500 mL Kuderna-Danish evaporative flask.
j. 10 mL graduated Kuderna-Danish concentrator tube.
k. Continuous extractor, one piece, glass, obtained from Hawk Creek Laboratory, Glen Rock, Pa. or Perpetual Systems, Rockville, Md. (see Figure 1).
l. GC/MS, Finnigan MAT 4500, 70eV electron impact ionization.
m. GC/MS, Finnigan MAT 4023, 70eV electron impact ionization.
n. Fused silica capillary column, 25 m, 0.32 mm. id., 1.0 um film thickness, SB-Phenyl-5, Lee Scientific, Salt Lake City, Utah.
o. Fused silica capillary column, 30 m., 0.32 mm. id., 1.0 um film thickness, SPB-5 (5% diphenyl: 94% dimethyl: 1% vinyl polysiloxane phases), Supelco, Bellefonte, Pa.
p. Drummond pipet, 100 uL dispensing pipettor, Model #375, used for pipetting surrogate spike.
q. Gordon-Keeble pipet, 100 uL dispensing pipettor, used for pipetting matrix spike.
r. Finnigan MAT Incos GC/MS 4500 software, Rev 4.07.82
s. Finnigan MAT Incos GC/MS 4023 software, Rev. 3.1, 01/79 Rev. C.
t. Volumetric pipet, 1 mL.
u. Volumetric flask, 10 mL.
v. Milli-RO15 Millipore System.
w. Screw cap vials with teflon-faced silicone septa, 1.8 mL, Cat. Nos. 3-3286 (vials) and 3-3210 (caps and septa), Supelco, Bellefonte, Pa.

FIGURE 1. LIQUID-LIQUID EXTRACTOR



LL-1000

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V. PROCEDURE

A. Continuous Extraction
EPA Method 625 (Base/Neutral, Acid Extraction)

Eight deionized water aliquots were chlorinated to approximately 1 ppm total chlorine using Chlorox. The chlorine concentration was confirmed by using a Hach DPD kit (visual comparator method). The DPD method gave a concentration of 0.7 ppm total chlorine.

Sample 1 was a non-chlorinated deionized water blank. Two aliquots of one liter each were not dechlorinated (samples 2 and 3). Samples 4 and 5 were dechlorinated using sodium thiosulfate. Samples 6 and 7 were dechlorinated using sodium arsenite. Samples 8 and 9 were dechlorinated using L-ascorbic acid. The chlorinated aliquots were prepared in glass gallon jugs. They were then dechlorinated (samples 4-9) by adding approximately 2.5 grams (to excess) of each dechlorinating agent to the appropriate jug. Each jug was then mixed by vigorous manual shaking. This dechlorination step was verified by using a Hach DPD kit to test for total chlorine.

Extractions were performed by the continuous extraction technique. The flow rate in each extractor was $\simeq$ 6 mLs/minute. A Neslab Coolflow refrigerated recirculator was used to cool the condensers. The temperature of each condenser was 10-15^{o}C. All extractions were carried out in the dark to prevent possible photodecomposition of light-sensitive compounds.

200-300 mLs of methylene chloride were placed into each continuous extractor and 1000 mLs of prepared sample were added. Each one liter aliquot was adjusted to a pH >11 using 6N NaOH. 100 uL of surrogate was spiked into each aliquot. An additional 200 mLs of methylene chloride was added through the water sample, with overflow into the 500 mL boiling flask. The samples were then spiked with 100 uL of base/neutral matrix spike (below the surface of the water sample) and 100 uL of acid matrix spike (above the surface of the water sample), except samples 1 and 2, in which the acid matrix spike was spiked below the surface of the water. For sample 1 (method blank), 200 mLs of methylene chloride was added through the water sample and then the surrogate, base/neutral and acid matrix spikes were added in succession.

The surrogate spike mix (in acetone) contained the following compounds (at a concentration of 500 ug/mL, except 2,4,6-tribromophenol which was 1500 ug/mL): 2-fluorophenol; d_5-phenol; d_5-nitrobenzene; 2-fluoro-1,1'-biphenyl; 2,4,6-tribromophenol; and d_{14}-p-terphenyl. The water samples were spiked with 100 uL of the surrogate spike mix, resulting in a concentration of 50 ug/L for all compounds

except 2,4,6-tribromophenol which was 150 ug/L.

The acid matrix spike mix (in methanol) contained the following compounds each at a concentration of 1000 ug/mL: phenol; 4-chloro-3-methylphenol; 4-nitrophenol; 2-chlorophenol and pentachlorophenol. The water samples were spiked with 100 uL of acid matrix spike mix, resulting in a concentration of 100 ug/L.

The base/neutral matrix spike contained the following compounds (at a concentration of 500 ug/mL each, except for pyrene which was 100 ug/mL): 1,4-dichlorobenzene; n-nitroso-di-n-propylamine; 1,2,4-trichlorobenzene; acenaphthylene; 2,4-dinitrotoluene; di-n-butyl phthalate and pyrene. The water samples were spiked with 100 uL of base/neutral spike mix, resulting in a concentration of 50 ug/L for all compounds, except for pyrene which was 10 ug/L.

The initial base/neutral (pH>11) extraction time was 24 $\pm$ 2 hours. The pH was adjusted with 6N NaOH. The extraction was then carried out at a pH <2 for 24 $\pm$ 2 hours. A fresh boiling flask was added and the pH was adjusted using 6N H_2SO_4. After extraction, the base/neutral and acid solvent fractions were filtered through Na_2SO_4 and glass wool, and combined in a Kuderna-Danish apparatus. The extracts were concentrated to 1 mL methylene chloride in calibrated concentration tubes using the Kuderna-Danish technique. Micro Snyder columns were used for the final concentration step ($\simeq$ 5 mL to 1 mL). The temperature of the water bath used for concentration was 65-70^{o}C. Extracts were transferred to 1.8 mL screw cap/septa vials and stored in a freezer until GC/MS analysis.

A reference standard containing the surrogate and matrix spike compounds was prepared at the time of extraction. 100 uL each of the surrogate mix, acid matrix spike mix and base/neutral matrix spike mix were diluted to 1 mL methylene chloride in a volumetric flask. The sample extracts and the reference standard were placed into 1.8 mL screw cap/septa vials. Each vial was spiked with 10 uL of a 4000 ug/mL internal standard mix just prior to GC/MS analysis. This mix contained d_4-1,4-dichlorobenzene; d_8-naphthalene; d_{10}-acenaphthene; d_{10}-phenanthrene; d_{12}-chrysene; and d_{12}-perylene. Each internal standard had a resulting concentration of 40 ug/mL.

The extracts and reference standard were analyzed by capillary GC/MS (70eV electron impact). A Supelco SPB-5 fused silica column was employed in the Finnigan 4500 GC/MS and an SB-phenyl-5 Lee Scientific fused silica column was used in the Finnigan 4023 GC/MS. The GC oven temperature program for both instruments was: 30^{o}C for 2 minutes to 300^{o}C at 10^{o}C/minute. The mass range scanned was 35-450 amu, at a scan rate of 0.8 seconds/scan. Data was acquired

using centroid sampling.

The percent recovery of surrogate and matrix spikes was determined as follows:

$$\% \text{ Rec} = \frac{\text{ng measured in extract}}{\text{ng measured in reference}} \times 100$$

B. Continuous Extraction (Acid/Neutral, Base Extraction)

Part 1

A series of experiments was performed by first extracting the samples at pH <2, followed by an extraction at pH >11. It was found that this extraction order improved recovery of short-chain phthalate esters (7). Also, floc and emulsion formation was minimized, even for the continuous extractor method. All compounds, except the most basic ones such as aniline or benzidine, are extracted at a pH <2.

In these experiments, sodium thiosulfate and sodium arsenite were tested as dechlorinating agents. Chlorinated (1.5 ppm total chlorine) samples spiked with surrogate and matrix spike compounds were analyzed. The extraction procedure was similar to that listed under procedure A with the following exceptions:

a. Chlorine concentrations were 1.5 ppm.
b. Surrogates and matrix spikes were spiked into separate aliquots above the surface of the water.
c. 200 mL methylene chloride was added to the boiling flask directly, instead of being poured through the sample.
d. Samples were first extracted under acid conditions (pH <2), followed by a basic extraction (pH >11).
e. Acenaphthene, not acenaphthylene, was used as a matrix spike compound.

Part 2

In a similar experiment, L-ascorbic acid was tested as a dechlorinating agent. The extraction procedure was similar to that listed under procedure A with the following exception: Samples were first extracted under acid conditions (pH <2), followed by a basic extraction (pH >11).

C. Separatory Funnel Extraction
EPA Method 625 (Base/Neutral, Acid Extraction)

Part 1

Sodium thiosulfate, sodium arsenite and L-ascorbic acid

were tested as dechlorinating agents using Method 625 (1). One exception to Method 625 should be noted: the base/neutral and acid extracts were combined before concentration. The initial chlorine concentration was 2.2 ppm for the sodium arsenite and L-ascorbic acid extractions. The initial chlorine concentration for the sodium thiosulfate extraction was 1.3 ppm. 5 grams of each dechlorinating reagent (per 200 mLs of chlorinated sample) was used to reduce the chlorine. Each was added to extreme excess to test for the presence of interfering peaks.

Part 2

Method 625 (1) recommended the use of 80 mg of sodium thiosulfate per liter of sample. 200 mLs of a 1.3 ppm total chlorine aliquot was prepared and 160.9 mg of sodium thiosulfate was added to neutralize the chlorine. The extraction was performed as in EPA Method 625 (1), except that base/neutral and acid extracts were combined before analysis.

D. Recovery Of Nitrobenzene And 2,4-Dinitrotoluene From Chlorinated Extracts Using L-Ascorbic Acid As A Dechlorinating Agent

This experiment was performed to determine the recoveries of nitrobenzene and 2,4-dinitrotoluene under both acid/neutral and base/neutral conditions. The results of procedures A and B indicated that 2,4-dinitrotoluene was lost under base/neutral extraction conditions. It was decided to also test a related compound, nitrobenzene, to determine if a whole class of compounds (nitroaromatics) were affected. All extractions were performed by the continuous extraction method.

The following were extracted under base/neutral, acid extraction conditions.

1. A one liter deionized water blank.
2. A one liter deionized water blank containing 1.25 g L-ascorbic acid.
3. One liter deionized water chlorinated to 0.9 ppm total chlorine, 1.25 g L-ascorbic acid added as dechlorinating agent.
4. A duplicate of 3.

The following were extracted under acid/neutral base extraction conditions.

5. One liter deionized water chlorinated to 0.9 ppm total chlorine, 1.25 g L-ascorbic acid added as dechlorinating agent.

6. A duplicate of 5.

All samples were spiked with 100 uL of a standard containing 500 ug/mL each of nitrobenzene and 2,4-dinitrotoluene. A reference was also prepared by adding 100 uL of the standard to a 1 mL volumetric flask, and diluting to volume with methylene chloride. Percent recovery of the spike was determined by the following formula:

$$\% \text{ Rec.} = \frac{\text{ng measured in extract}}{\text{ng measured in reference}} \times 100$$

E. Recovery Of 2,4-Dinitrotoluene and 2,6-Dinitrotoluene From Chlorinated Extracts Using L-Ascorbic Acid As A Dechlorinating Agent

This procedure was performed to determine the recoveries of 2,4-dinitrotoluene and 2,6-dinitrotoluene under base/neutral extraction conditions using both excess (3.3 g/L) and low levels (80 mg/L) of L-ascorbic acid. 80 mg is the quantity recommended by EPA Method 625 for sodium thiosulfate addition. All extractions were performed by the continuous extraction method.

The following were extracted:

1. One liter deionized water.
2. One liter deionized water blank chlorinated to 0.6 ppm total chlorine, 80 mg of L-ascorbic acid added as dechlorinating agent.
3. A duplicate of 2.
4. One liter deionized water chlorinated to 0.6 ppm total chlorine, 80 mg of L-ascorbic acid added as a dechlorinating agent. (Analyzed in quadruplicate).
5. One liter deionized water chlorinated to 0.6 ppm total chlorine, 3.26 g of L-ascorbic acid added as a dechlorinating agent.

Samples 1, 4 and 5 were spiked with 100 uL of each of the following:

500 ug/mL 2,6-dinitrotoluene
Base/neutral matrix spike mix (containing 500 ug/mL 2,4-dinitrotoluene)

A reference was also prepared by adding 100 uL of each standard to a 1 mL volumetric flask, and diluting to volume with methylene chloride. Percent recovery of the spike was determined by the following formula:

$$\% \text{ Rec} = \frac{\text{ng measured in extract}}{\text{ng measured in reference}} \times 100$$

F. Comparison Study Using 20 and 80 mg/L of Sodium Thiosulfate As A Dechlorinating Agent

This study was performed to compare the recommended level of sodium thiosulfate (80 mg per liter of sample as stated in Method 625) with a lower level, 20 mg/L. Both levels were tested using continuous extraction. Separatory funnel extraction was used to test recoveries at the 80 mg level only.

The following tests were performed:

1. Continuous extraction using 80 mg/L sodium thiosulfate
2. Continuous extraction using 20 mg/L sodium thiosulfate
3. Separatory funnel extraction using 80 mg/L sodium thiosulfate.

In each test, the following were analyzed:

1. A one liter deionized water aliquot spiked with surrogate and matrix spike compounds and extracted under acid/neutral, base conditions.
2. A duplicate of 1.
3. A one liter deionized water aliquot spiked with surrogate and matrix spike compounds and extracted under base/neutral, acid conditions.
4. A duplicate of 3.

The residual chlorine concentration was 1.6 ppm for the 80 mg/L tests and was 1.8 ppm for the continuous extraction analysis using 20 mg/L sodium thiosulfate.

A reference was also prepared by adding 100 uL of each standard to a 1 mL volumetric flask, and diluting to volume with methylene chloride. Percent recovery of the spike was determined by the following formula:

$$\% \text{ Rec} = \frac{\text{ng measured in extract}}{\text{ng measured in reference}} \times 100$$

VI. GENERAL QUALITY CONTROL

a. All glassware, sodium sulfate and glasswool used in this experiment was previously muffled at 450°C for 3-4 hours.

b. All surrogate, base/neutral and acid matrix spike standards were traceable to the Quality Assurance Materials Bank in Research Triangle Park, N. C. The internal standard mix was obtained from Supelco, Bellefonte, Pa.

c. Each GC/MS was calibrated with FC43 prior to analysis.

d. Each GC/MS was tuned by obtaining the spectrum of DFTPP. All mass assignments and relative abundances were found to be in acceptable ranges or the instruments were adjusted until suitable spectra were obtained.

e. Immediately before analysis, each sample was spiked with an internal standard mixture, including d_{10}-phenanthrene. All quantitation was done using d_{10}-phenanthrene as the internal standard.

f. The sensitivity of each instrument to 40 ng of d_{10}-phenanthrene was as follows:

Finnigan 4500 GC/MS : 80,000 area counts (average)
Finnigan 4023 GC/MS : 110,000 area counts (average)

g. All surrogate and matrix spike recovery limits referenced in this study were from the Superfund Contract Laboratory Program (CLP) protocols (8).

h. All recoveries were compared against a reference standard prepared the same day the samples were extracted. Reference standards and samples were analyzed on the same day and on the same GC/MS.

i. Data quantitation was performed by automated procedures using Incos software (Finnigan MAT, San Jose, California).

j. Matrix spike and surrogate compound identifications were made by comparing known reference spectra to those of the unknowns. Other compound identifications, such as contaminant peaks associated with certain L-ascorbic acid additions, were made using the EPA-NIH spectral library.

VII. EXPERIMENT-SPECIFIC QUALITY CONTROL

Procedure A Continuous Extraction EPA Method 625 (1)
(Base/Neutral, followed by Acid Extraction)

1. A deionized water blank was extracted along with the samples. Two chlorination blanks were also extracted (1000 mLs deionized water, chlorinated using Chlorox, with no dechlorination agent added).

2. Each sample, except the deionized water blank, was analyzed in duplicate.

3. Blanks and the reference standard were run on both instruments. References were run at the start and end of each day's analyses, except on one day when only two analyses were performed. In this case, a single reference was run between the two analyses.

Procedure B Continuous Extraction
(Acid/Neutral, followed by Base Extraction)

1. A deionized water blank was extracted. Two chlorination blanks were also extracted (one was spiked with surrogates, the other with matrix spike compounds).

2. L-ascorbic acid analyses were performed in duplicate. All other tests represent a single analysis.

3. Blanks and the reference standard were run on both instruments. References were either run at the start and end of each day's analyses, or a single reference was run just prior to the sample analyses.

Procedure C Separatory Funnel Extraction
EPA Method 625 (1)
(Base/Neutral, followed by Acid Extraction)

1. A method blank was analyzed with each set of analyses.

Procedure D Recovery of Nitrobenzene and 2,4-Dinitrotoluene From Chlorinated Extracts Using L-Ascorbic Acid As A Dechlorinating Agent

1. A method blank was analyzed (base/neutral extraction).

2. A non-chlorinated blank containing L-ascorbic acid was analyzed (base/neutral extraction).

3. A reference was analyzed before the extracts.

4. All samples except blanks were analyzed in duplicate.

Procedure E Recovery of 2,4-Dinitrotoluene and 2,6-Dinitrotoluene From Chlorinated Extracts Using L-Ascorbic Acid As A Dechlorinating Agent

1. A control containing no added chlorine or L-ascorbic acid was spiked and analyzed.

2. Two chlorinated blanks containing 80 mg/L of L-ascorbic acid were analyzed.

3. The analysis as described under number 4 of procedure E was performed in quadruplicate.

4. A reference was analyzed before the extracts.

Procedure F Comparison Study Using 20 and 80 mg/L of Sodium Thiosulfate As A Dechlorinating Agent

1. Each extraction was performed in duplicate.

2. A reference was analyzed along with the extracts.

VIII. RESULTS AND DISCUSSION

Effects of Chlorination

The effects of chlorination on the surrogate and matrix spike compounds were determined. As shown in Table 1, the recovery of d_5-phenol under base/neutral, acid extraction conditions using the continuous extraction method was 8.45%. This loss of d_5-phenol was reflected in the observation of the chlorination product, d_5-chlorophenol.

Similar results were encountered for the matrix spike compounds. Extracting the matrix spike compounds in the presence of chlorine (samples 2 and 3 under base/neutral conditions) caused reactions to occur which decreased the concentration of phenol and 4-chloro-3-methylphenol. The average recoveries for phenol and 4-chloro-3-methylphenol were 9.4% and 33.65% respectively (Table 2). The products formed by the chlorination of these compounds were as follows: 2,4-dichlorophenol; 2,6-dichlorophenol; 3-chlorophenol; 2,4-dichloro-6-methylphenol; and 2-chlorophenol.

The effect of chlorination would be expected to be intensified under acidic extraction conditions (pH < 2), since most of the chlorine would be in the free reactive state (6). Under basic conditions, most of the chlorine would be present as hypochlorite ion (6).

$$Cl_2 + H_2O \underset{pH<4}{\overset{pH>4}{<==>}} HCl + HOCl$$

$$HOCl \underset{pH<9}{\overset{pH>9}{<==>}} H^+ + OCl^-$$

Increased chlorination products of the matrix spike compounds were observed under acid/neutral conditions. These included: 2,4-dichlorophenol; 3-chlorophenol; 2,6-dichlorophenol; 1,2,3-trichlorobenzene; 2,4-dichloro-6-methylphenol; 3,4,6-trichloro-o-cresol; 2-chlorophenol; chloroacenaphthene; dichloroacenaphthene and chloropyrene. (It should be noted that the matrix spike mix used for the acid/neutral extraction included acenaphthene instead of acenaphthylene).

Matrix spike recoveries for acid/neutral extraction are given in Table 4. It should be noted that phenol, 4-chloro-3-methylphenol, acenaphthene and pyrene showed significant recovery losses under these conditions. The recovery of the surrogate d_5-phenol was only 0.7% (Table 3).

TABLE 1

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)

EXTRACTS

COMPOUND	BLANK	CHLORINATED EXTRACT	SODIUM THIOSULFATE	SODIUM ARSENITE	L-ASCORBIC ACID	CLP LIMITS (WATER)
2-FLUOROPHENOL	71.4	45.2	51.7	70.05	80.35	21-100
D5-PHENOL	77.8	8.45	59.5	77.05	85.35	10-94
D5-NITROBENZENE	87.1	76.5	61	80.05	87.85	35-114
2-FLUORO-1,1'-BIPHENYL	87.5	61.65	53.2	64.05	74.2	43-116
2,4,6-TRIBROMOPHENOL	81.8	72.95	68	85.25	93.25	10-123
D14-P-TERPHENYL	88.1	84.9	69.35	91.9	97.05	33-141

BLANK RESULTS REPRESENT ONE ANALYSIS.
ALL OTHER RESULTS ARE AVERAGES OF DUPLICATE ANALYSES.

TABLE 2

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

MATRIX SPIKE RECOVERY
(REPORTED AS %)

COMPOUND	EXTRACT					
	BLANK	CHLORINATED EXTRACT	SODIUM THIOSULFATE	SODIUM ARSENITE	L-ASCORBIC ACID	CLP LIMITS (WATER)
PHENOL	84.7	9.4	61.1	80	87.9	12-89
2-CHLOROPHENOL	87.9	105.7	62.55	79.95	79.85	27-123
1,4-DICHLOROBENZENE	90.7	75.6	63.95	84.05	88.2	36-97
N-NITROSODI-N-PROPYLAMINE	92.9	76.8	66.35	85.8	91.55	41-116
1,2,4-TRICHLOROBENZENE	90.6	81.1	66.25	84.15	86.35	39-98
4-CHLORO-3-METHYLPHENOL	91.6	33.65	68.15	85.7	92.15	23-97
ACENAPHTHYLENE	99.1	87.8	72.65	91.5	89.9	46-118
4-NITROPHENOL	71.2	66.75	70.2	85.05	97.25	10-80
2,4-DINITROTOLUENE	93.5	79.65	71.4	90.3	60.75	24-96
PENTACHLOROPHENOL	61.1	55.65	64.65	80.85	106.5	9-103
DIBUTYLPHTHALATE	21.6	34.7	30.95	50.65	57.95	11-117
PYRENE	92.1	82.65	69.6	91.35	95.05	26-127

BLANK RESULTS REPRESENT ONE ANALYSIS.
ALL OTHER RESULTS ARE AVERAGES OF DUPLICATE ANALYSES.

TABLE 3

EXPERIMENT B: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)

EXTRACTS

COMPOUND	BLANK	CHLORINATED EXTRACT	SODIUM ARSENITE	SODIUM THIOSULFATE	L-ASCORBIC ACID	CLP LIMITS (WATER)
2-FLUOROPHENOL	93.2	52.4	68.7	55.7	79.8	21-100
D5-PHENOL	83.9	0.7	55.9	46.8	81.1	10-94
D5-NITROBENZENE	92	85	79.6	62.9	84.7	35-114
2-FLUORO-1,1'-BIPHENYL	90.7	84.4	81.5	67.9	72.5	43-116
2,4,6-TRIBROMOPHENOL	90.5	69.3	69.3	53.5	84	10-123
D14-P-TERPHENYL	97.6	87.2	88.9	75.9	86.5	33-141

RESULTS FOR L-ASCORBIC ACID ARE AVERAGES OF DUPLICATE ANALYSES.
ALL OTHER RESULTS REPRESENT ONE ANALYSIS.

Our laboratory currently uses methylene chloride that contains cyclohexene as a preservative. The purpose of this additive is to scavenge any HCl present in the solvent. This additive has been detected in samples and blanks, along with the following related compounds: cyclohexanone; 2-cyclohexen-1-one; and 2-cyclohexen-1-ol. Extracted samples that contained chlorine have produced the following derivatives of cyclohexene: chlorocyclohexene; dichlorocyclohexane; chlorocyclohexanone; and 3,3,3-trichloro-1-propene.

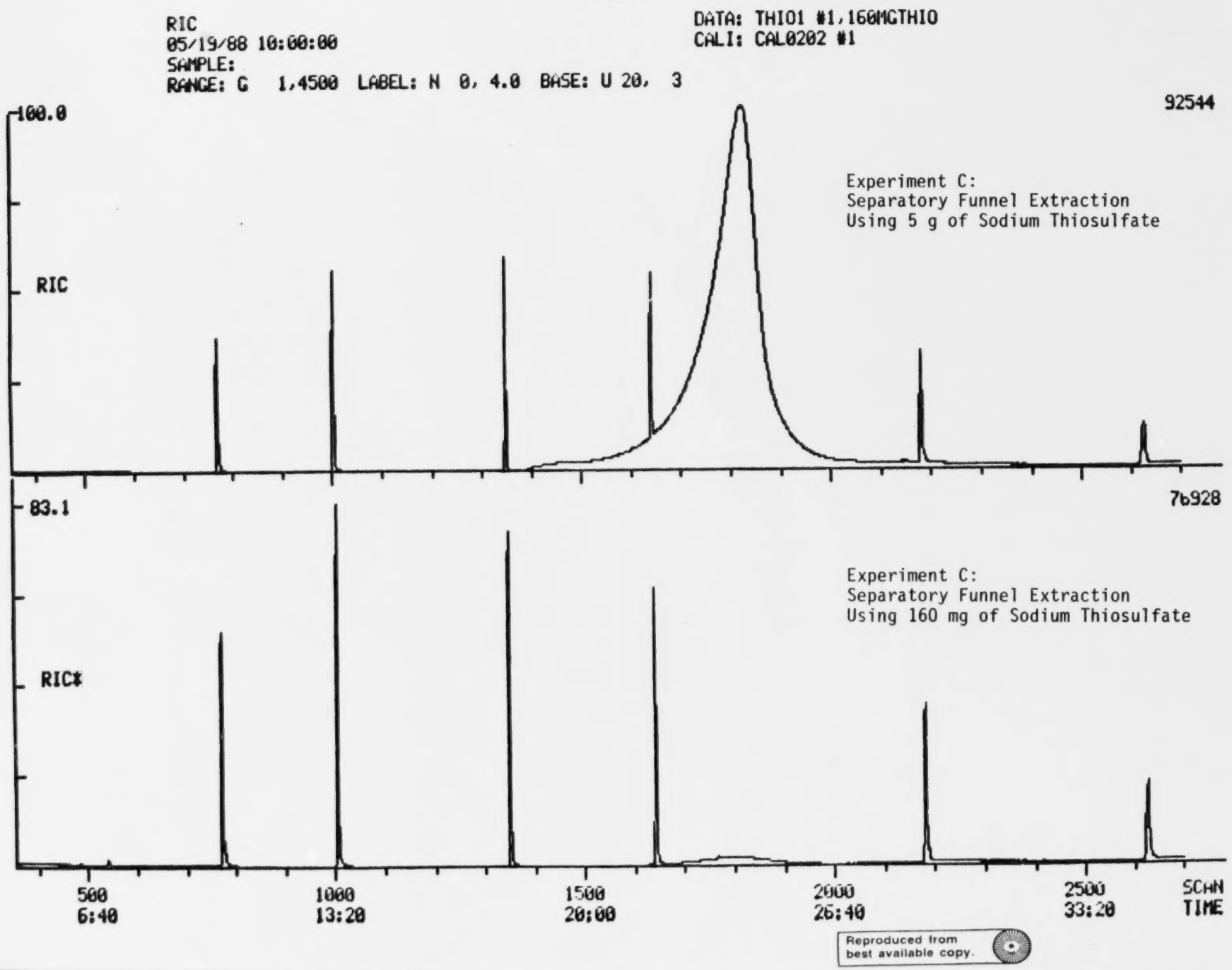
Sodium Thiosulfate

Sodium thiosulfate, sodium arsenite and L-ascorbic acid were tested to determine their suitability as dechlorinating agents. Sodium thiosulfate, the compound required by Method 625 (1) for dechlorinating waste effluents, was the least suitable reagent tested when excess amounts were used. It is stated in this method that sodium thiosulfate is to be added in the field. Field conditions are difficult to control and it is conceivable that excess amounts could be added. Method 625 (1) specified that 80 mg of sodium thiosulfate per liter of sample should be added to neutralize the chlorine. No analytical problems were encountered when this amount was used for separatory funnel extraction. However, a significant molecular sulfur peak was obtained using 80 mg of sodium thiosulfate per liter of sample under continuous extraction conditions. It should be emphasized that all observations concerning the testing of the three dechlorinating agents were made when excess amounts of each were used.

With the exception of 2,4-dinitrotoluene, recoveries of matrix and surrogate spike compounds were lowest for those samples dechlorinated with sodium thiosulfate (Tables 1 and 2). These lower recoveries may be due to the large number of sulfur crystals which formed in the concentrator tube during the Kuderna-Danish process. It is possible that matrix and surrogate spike compounds became trapped in the sulfur crystals, resulting in lower recoveries.

Chromatographic problems were also encountered with sodium thiosulfate. A large molecular sulfur peak eluted at 1500-1850 scans (RRT of 0.990 - 1.145, relative to d_{10}-phenanthrene). Figure 2 shows the large sulfur peak formed as a result of using an excess (5 g) amount of sodium thiosulfate for dechlorination (upper chromatogram). When 160 mg was used (lower chromatogram), the sulfur peak was still detected, but at a level that would not cause any analytical problems. The six sharp peaks appearing in both chromatograms in figure 2 are internal standards. The dual chromatogram comparison contrasts the effect of excess sodium

Figure 2



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thiosulfate with an amount near the recommended level (80 mg). The molecular sulfur peak (formed when excess amounts of sodium thiosulfate are used) co-elutes with the following compounds: bromophenoxybenzene, hexachlorobenzene, pentachlorophenol, d_{10}-phenanthrene (internal standard), phenanthrene, anthracene, di-n-butyl phthalate and fluoranthene. However, quantitation was not affected since no interference was observed with the quantitation ions (base peaks) used for each compound. Identification of the above listed compounds would have to be made by subtracting the molecular sulfur spectrum (Figure 2A) from the total spectrum. Another interferent, hexathiepane, had a relative retention time of 0.975. It did not co-elute or interfere with the analysis of any semi-volatile compound listed under EPA Method 625 (1).

The problems cited above with the use of sodium thiosulfate occurred as a result of the acidic extraction of the test samples. Under acidic conditions, sodium thiosulfate is unstable and undergoes the following decomposition and disproportionation reactions (2):

1. $S_2O_3^{-2} \rightarrow S_{(s)} + SO_3^{-2}$

   Decomposition/disproportionation of thiosulfate to sulfur and sulfite ion.

2. $2S_2O_3^{-2} \rightarrow S_{(s)} + 3SO_2 + 4e^-$

   Decomposition/disproportionation of thiosulfate to sulfur and sulfur dioxide (2,9).

Equation 2 probably represents the SO_2 source which is reported to cause interferences with GC/MS analysis using purge and trap (excess sodium thiosulfate under acidic conditions) (4).

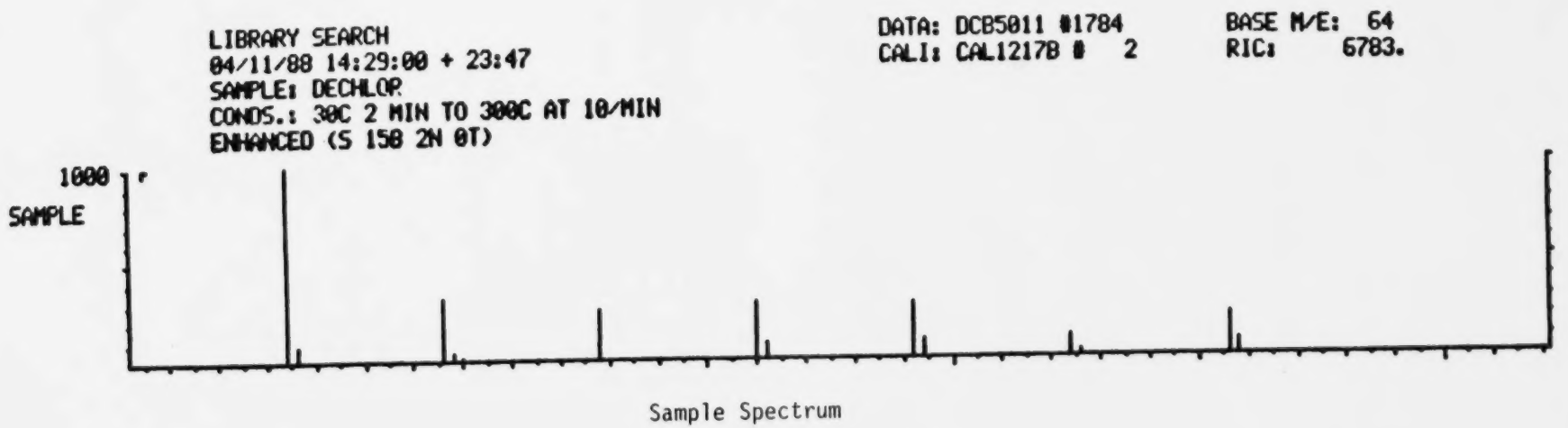
Under acidic conditions, a colloidal solution of sulfur is stabilized by the acid (9). Reactions 1 and 2 do not occur under slightly acidic, neutral or basic conditions. Thiosulfate is stable under these conditions, and forms the tetrathionate ion (2):

$$2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2e^-$$

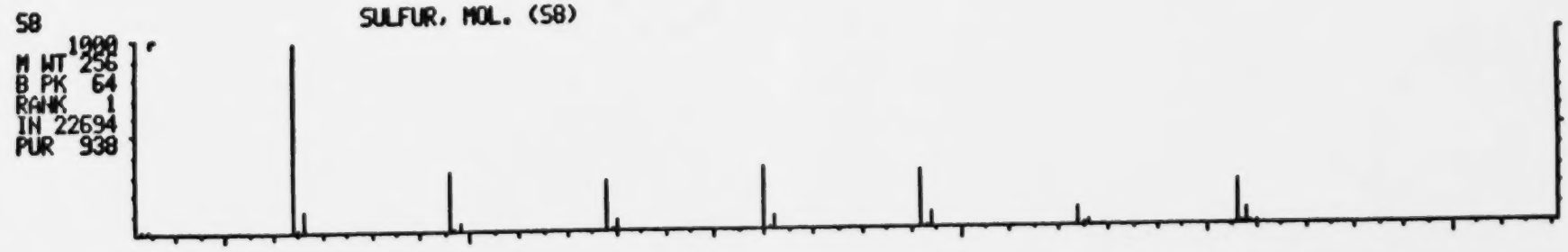
The sulfur detected by GC/MS analysis and observed in this work is molecular sulfur (S_8). After elemental sulfur has been formed as a result of acid extraction, a polymerization reaction occurs to form the S_8 molecule. The structure of this molecule is known as a "puckered ring" (2).

Sodium thiosulfate reduces chlorine according to the following equation (9):

Figure 2A



Sample Spectrum



NBS Library Spectrum

$$Na_2S_2O_3 + H_2O + Cl_2 = Na_2SO_4 + S + 2HCl$$

Elemental sulfur is produced as a result of the reduction of chlorine by sodium thiosulfate. The amount of sulfur produced would be directly proportional to the amount of chlorine. In this work, chlorine concentrations of between 0.6 and 2.2 ppm were used. Thus, the amount of sulfur produced as a result of this reaction would also be in this range. However, most of the sulfur that caused chromatographic problems in these experiments was formed under acidic extraction conditions as detailed above (decomposition/disproportionation reactions). This resulted from the addition of excess sodium thiosulfate in gram quantities.

The continuous extraction acid/neutral, base extraction scheme gave greater recoveries than for base/neutral, acid extraction for all matrix spike compounds except 4-nitrophenol (Tables 2 and 4). Surrogate recoveries (Tables 1 and 3) did not exhibit any general trend toward favoring one or the other. All raw data for sodium thiosulfate can be found in Tables 2A and 6A in the Appendix.

Sodium Arsenite

Sodium arsenite produced the cleanest chromatogram of the three compounds tested. Figure 3 (upper chromatogram) showed the result when an excess (5 g) of sodium arsenite was used as the dechlorinating reagent (separatory funnel extraction). A small unknown peak eluting just before the third internal standard, d_{10}-acenaphthene, was too small to be quantitated by the Incos software. Figure 4 compared the two dechlorinating reagents, sodium thiosulfate and sodium arsenite, in a dual chromatogram display. In each case, excess amounts were used (2.5 g, continuous extraction). The molecular sulfur peak was prominent in the sodium thiosulfate chromatogram; the interference peak mentioned above for sodium arsenite was a very small peak, just above the detection level, and not appearing in the lower chromatogram. The sharp peaks that appeared in the chromatograms were internal standards, surrogates and matrix spike compounds.

Sodium arsenite gave acceptable results for all spike components (Tables 1 and 2). The percent recovery for di-n-butyl phthalate was low: 50.65% using continuous extraction under base/neutral, acid extraction conditions. However, recoveries for all three dechlorinating agents were low for this compound under these conditions. This is due to the fact that certain phthalates hydrolyze under basic conditions (7). With the exception of di-n-butyl phthalate, all other compounds gave similar recoveries when the two extraction schemes were compared for the continuous extraction method (sodium arsenite dechlorination). Results for acid/neutral extraction are shown in Tables 3 and 4. The raw data for sodium arsenite may be found in Tables 3A and 7A in

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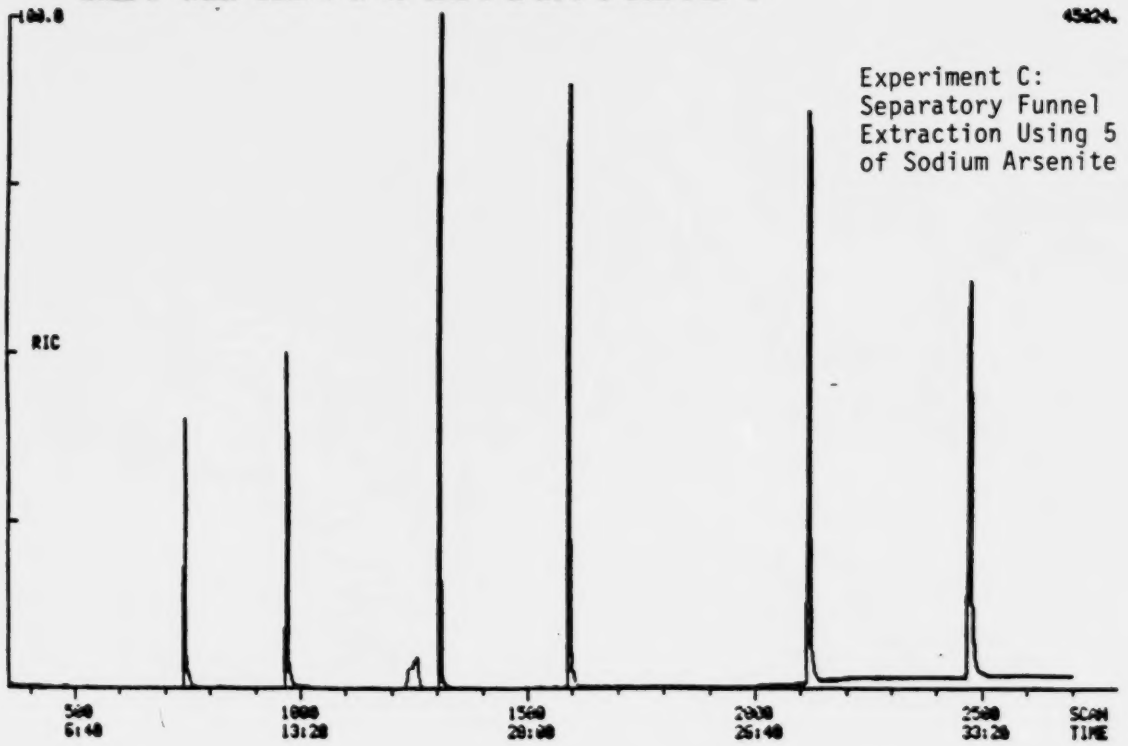
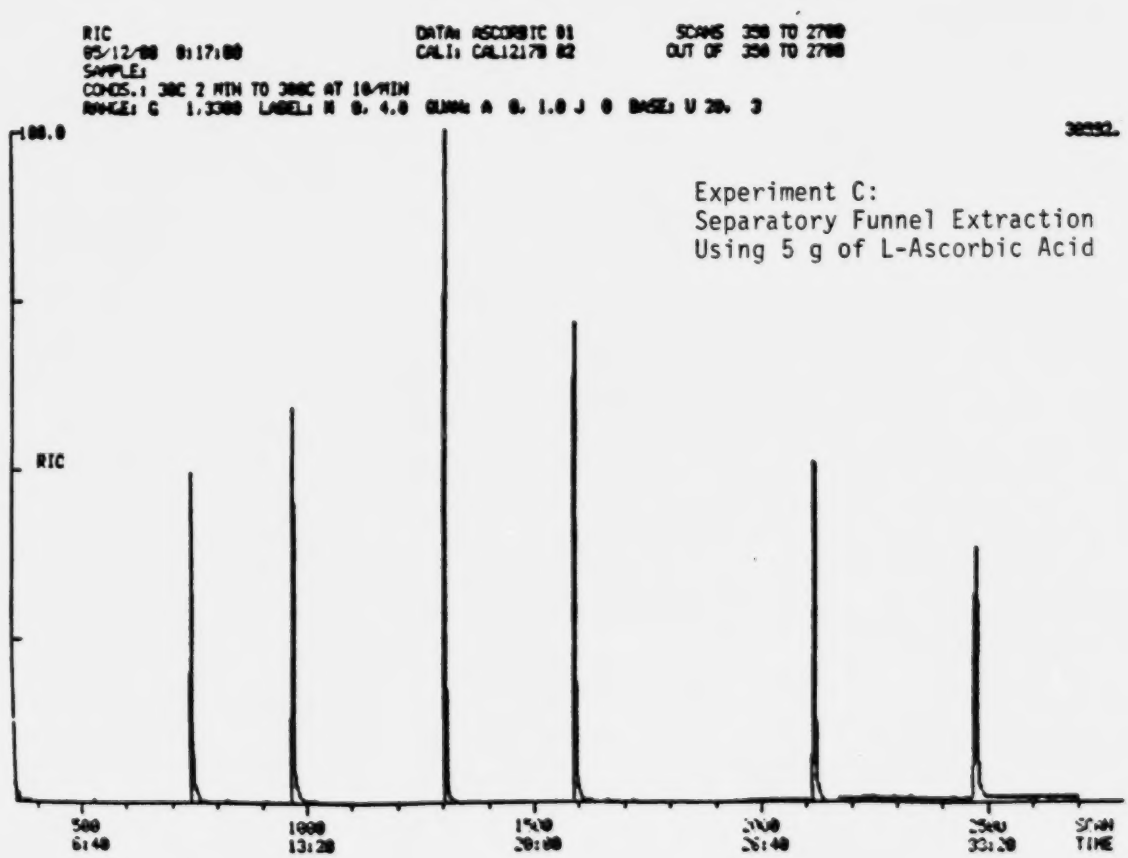
Figure 3



Experiment C:
Separatory Funnel
Extraction Using 5 g
of Sodium Arsenite



Experiment C:
Separatory Funnel Extraction
Using 5 g of L-Ascorbic Acid

Figure 4

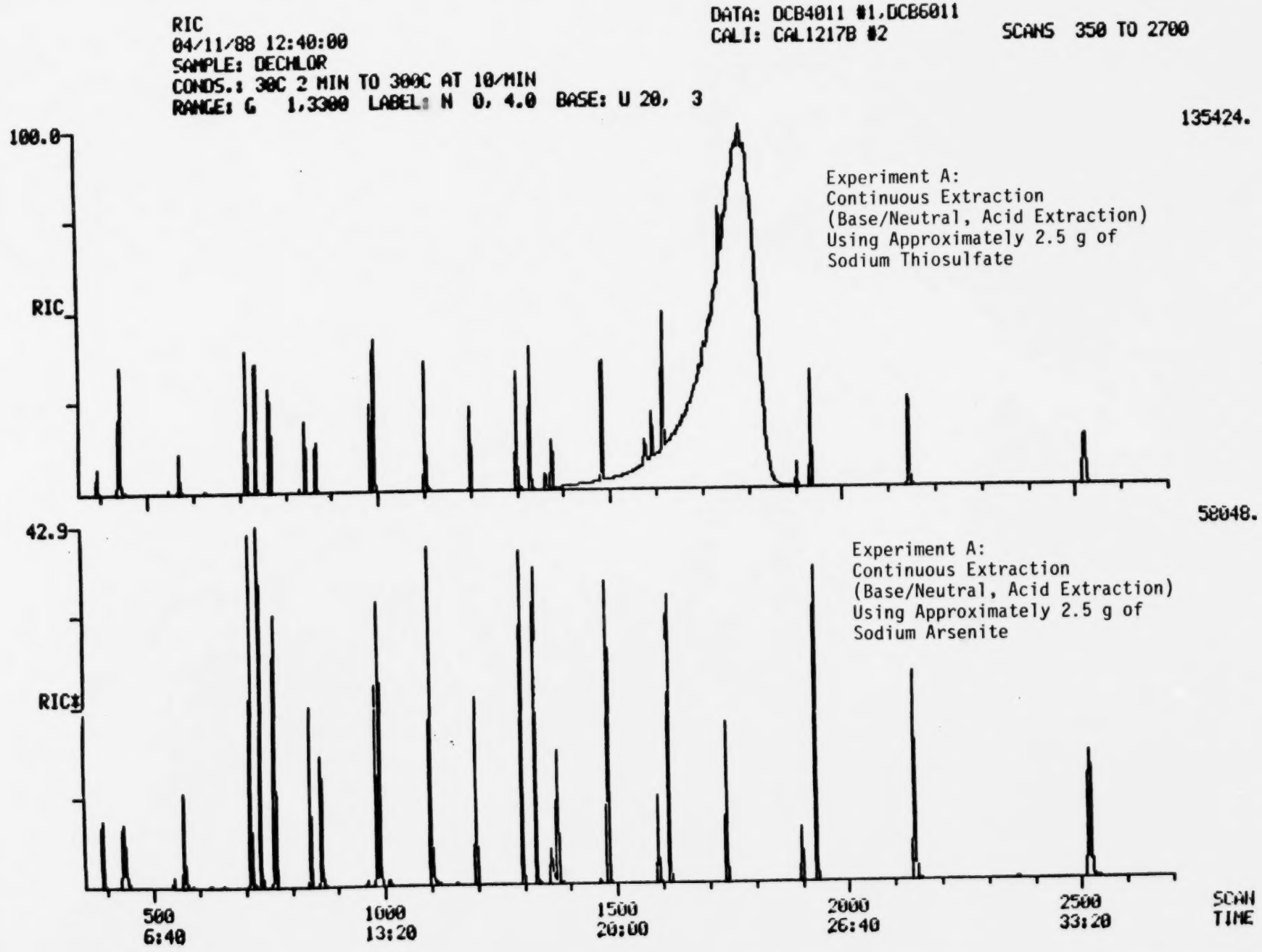

RIC
04/11/88 12:40:00
SAMPLE: DECHLOR
CONDS.: 30C 2 MIN TO 300C AT 10/MIN
RANGE: G 1,3300 LABEL: N 0, 4.0 BASE: U 20, 3
DATA: DCB4011 #1,DCB6011
CALI: CAL1217B #2
SCANS 350 TO 2700
135424.
100.0
RIC
Experiment A:
Continuous Extraction
(Base/Neutral, Acid Extraction)
Using Approximately 2.5 g of
Sodium Thiosulfate
58048.
42.9
RIC
Experiment A:
Continuous Extraction
(Base/Neutral, Acid Extraction)
Using Approximately 2.5 g of
Sodium Arsenite
500
6:40
1000
13:20
1500
20:00
2000
26:40
2500
33:20
SCAN
TIME

TABLE 4

EXPERIMENT B: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

MATRIX SPIKE RECOVERY
(REPORTED AS %)

COMPOUND	EXTRACT					
	BLANK	CHLORINATED EXTRACT	SODIUM THIOSULFATE	SODIUM ARSENITE	L-ASCORBIC ACID	CLP LIMITS (WATER)
PHENOL	99.6	9.9	78.1	86.9	86.5	12-89
2-CHLOROPHENOL	100	107	76.7	86.5	86.1	27-123
1,4-DICHLOROBENZENE	94	82.3	65.6	81	86.7	36-97
N-NITROSODI-N-PROPYLAMINE	102	85.6	78.9	86.6	90.3	41-116
1,2,4-TRICHLOROBENZENE	92	86	69.3	83.6	87	39-98
4-CHLORO-3-METHYLPHENOL	102	19.4	75.8	85	88.6	23-97
ACENAPHTHYLENE/ACENAPHTHENE	98	13.8	79	88.1	89.1	46-118
4-NITROPHENOL	94	88.7	69.2	80.2	88.9	10-80
2,4-DINITROTOLUENE	103	96.4	77.8	85.4	91	24-96
PENTACHLOROPHENOL	80	133	94.5	94.3	94.5	9-103
DIBUTYLPHTHALATE	101	98.6	95.7	92.2	92	11-117
PYRENE	103	40.8	85.9	88.2	92.3	26-127

RESULTS FOR L-ASCORBIC ACID ARE AVERAGES OF DUPLICATE ANALYSES.
ALL OTHER RESULTS REPRESENT ONE ANALYSIS.

the Appendix.

Sodium arsenite (Na_3AsO_3 or $NaAsO_2$) is a white, water-soluble powder. It reduces chlorine according to the following equation (9):

$$\underset{\text{Arsenite}}{AsO_3^{-3}} + Cl_2 + H_2O = \underset{\text{Arsenate}}{AsO_4^{-3}} + 2HCl$$

This reaction does not proceed under strongly acidic conditions, since the arsenite would then be converted to arsenious acid, a non-reducing agent (9).

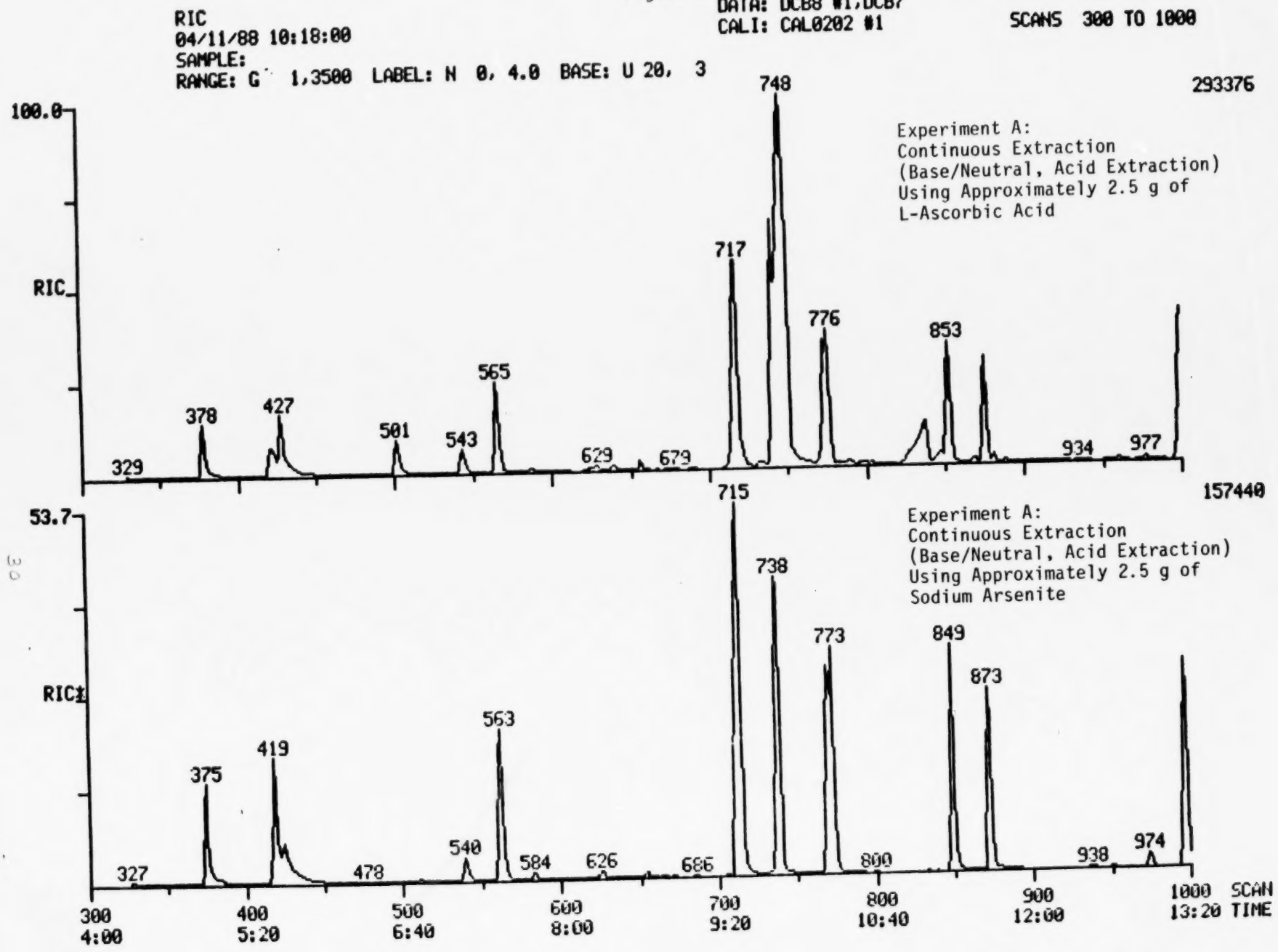
No analytical or chromatographic problems were encountered with sodium arsenite. It is, however, very toxic. The probable oral lethal dose for humans is less than 5 mg/kg (3).

L-Ascorbic Acid

L-ascorbic acid gave the highest recoveries for the surrogate spike compounds and for most of the matrix spike compounds except 2-chlorophenol, acenaphthylene and 2,4-dinitrotoluene (Tables 1 and 2, continuous extraction, base/neutral, acid extraction conditions). Chromatographic interferences were observed at relative retention times of 0.307, 0.453, 0.509, 0.527 and 0.606, relative to d_{10}-phenanthrene. These five peaks corresponded to the following compounds respectively: 2-furancarboxaldehyde, $C_5H_4O_2$, CAS No. 98-01-1; an unidentified compound, with base peak of m/z 55; 2-furancarboxylic acid, $C_5H_4O_3$, CAS No. 88-14-2; 3-furancarboxylic acid, methyl ester, $C_6H_6O_3$, CAS No. 13129-23-2; and 4H-pyran-4-one, 3,5-dihydroxy-2-methyl, $C_6H_6O_4$, CAS No. 1073-96-7. 2-furancarboxylic acid would interfere with the quantitation of bis(2-chloroisopropyl) ether. The quantitation ion, 45, was present in the spectrum of 2-furancarboxylic acid. For other peaks eluting at this time (benzenemethanol, 2-methylphenol and 4-methylphenol), quantitation was not affected. 2-furancarboxaldehyde and 3-furancarboxylic acid, methyl ester did not interfere in the analysis of semivolatiles. 4H-pyran-4-one, 3,5-dihydroxy-2-methyl eluted near 1,2,4-trichlorobenzene, but did not interfere with quantitation. The unknown peak eluted near 2-chlorophenol, but did not interfere with quantitation.

These interferences are observed in Figure 5 in the upper chromatogram. The lower chromatogram provides a comparison with sodium arsenite. The major difference was the large interference peak at scan 748 (RRT = .453) in the L-ascorbic chromatogram. This peak could not be identified. Figure 3 (lower chromatogram) showed the chromatogram re-

Figure 5


RIC
04/11/88 10:18:00
SAMPLE:
RANGE: G 1,3500 LABEL: N 0, 4.0 BASE: U 20, 3
DATA: DCB8 #1,DCB7
CALI: CAL0202 #1
SCANS 300 TO 1000
293376
100.0
RIC
748
717
776
853
565
378
427
501
543
329
629
679
934
977
Experiment A:
Continuous Extraction
(Base/Neutral, Acid Extraction)
Using Approximately 2.5 g of
L-Ascorbic Acid
157440
53.7
RIC
715
738
773
849
873
563
419
375
540
584
626
686
327
478
800
938
974
Experiment A:
Continuous Extraction
(Base/Neutral, Acid Extraction)
Using Approximately 2.5 g of
Sodium Arsenite
300
4:00
400
5:20
500
6:40
600
8:00
700
9:20
800
10:40
900
12:00
1000 SCAN
13:20 TIME

sulting when an excess amount (5 g) of L-ascorbic acid is added and extracted using a separatory funnel. No interference peaks were observed, as they were when continuous extraction was employed. Continuous extraction gave better recoveries for all compounds (Tables 1 and 2), including interference peaks.

The reduction of chlorine by L-ascorbic acid is represented by the following equation (10):

$$\underset{\text{L-ascorbic acid}}{C_6H_8O_6} + Cl_2 = \underset{\text{L-dehydro-ascorbic acid}}{C_6H_6O_6} + 2HCl$$

Under basic conditions, L-dehydroascorbic acid is converted to L-diketogulonic acid ($C_6H_8O_7$) (11).

Using the continuous extraction method under base/neutral extraction conditions, recoveries of 2,4-dinitrotoluene from a matrix spike were much lower (60.75%) than for any other agent or blank tested (Table 2). In a similar experiment (procedure D, spiking with nitrobenzene and 2,4-dinitrotoluene), an average recovery of 30.1% was obtained for 2,4-dinitrotoluene (Table 5). The recovery was probably lower due to the larger amount of L-ascorbic used (5 g as compared to 2.5 g in procedure A).

In procedure E, the recoveries of 2,4-dinitrotoluene and 2,6-dinitrotoluene were determined under base/neutral, acid extraction conditions, using both excess and low (80 mg per liter of sample, the recommended level of sodium thiosulfate as specified in Method 625) levels of L-ascorbic acid. Results are reported in Table 6. When 80 mg of L-ascorbic acid per liter of sample was used as the dechlorinating agent, good recoveries of both compounds were obtained. Recoveries were similar to those of a spiked control blank. However, when excess amounts (3.3 g/L) of L-ascorbic acid were used for dechlorination, recoveries for both compounds were lower as compared to the control. The recovery of 2,4-dinitrotoluene was 41%; 2,6-dinitrotoluene was recovered at 80.4% (as opposed to recoveries of 96.6 and 93.5 respectively for the control). Under acid/neutral extraction conditions using a continuous extractor and approximately 2.5 g of L-ascorbic acid, the average recovery of 2,4-dinitrotoluene was 91% (Table 4). Raw data for L-ascorbic acid may be found in Tables 4A, 4B, 8A, 8B, 9A and 10A in the Appendix.

It may be possible that L-diketogulonic acid (the form of L-ascorbic acid under basic conditions) reacted with 2,4-dinitrotoluene. However, no reaction products were detected. It has been found that o-nitrotoluene reacts with galactose, fructose or mannose under basic conditions at a temperature of 80-90°C to form 2,2'-dimethylazoxybenzene ($C_{14}H_{20}N_2O$) (12). Possibly, 2,4-dinitrotoluene could have been converted

TABLE 5

EXPERIMENT D: CONTINUOUS EXTRACTION

AROMATIC NITRO COMPOUND RECOVERY
(REPORTED AS %)
DECHLORINATION USING 1.25 G L-ASCORBIC ACID

		EXTRACTS			
COMPOUND	BLANK	BLANK + ASCORBIC ACID	BASE/NEUTRAL (AVERAGE)	ACID/NEUTRAL (AVERAGE)	CLP LIMITS (WATER)
2,4-DINITROTOLUENE	94	33.9	30.1	96.7	24-96
NITROBENZENE	103.5	106.1	98.5	105.7	NA1

BLANKS WERE NOT CHLORINATED
BLANKS WERE EXTRACTED UNDER BASE/NEUTRAL CONDITIONS
B/N AND A/N EXTRACTS WERE CHLORINATED TO 0.9 PPM TOTAL CHLORINE

TABLE 6

EXPERIMENT E: CONTINUOUS EXTRACTION
BASE/NEUTRAL, ACID EXTRACTION

DINITROTOLUENE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

EXTRACTS

COMPOUND	BLANK	3.3 G/L L-ASCORBIC ACID (SINGLE VALUE)	80 MG/L L-ASCORBIC ACID (AVERAGE)	CLP LIMITS (WATER)
2,4-DINITROTOLUENE	96.6	41	91.8	24-96
2,6-DINITROTOLUENE	93.5	80.4	90.1	NA‡

BLANK WAS NOT CHLORINATED
ALL OTHER SAMPLES WERE CHLORINATED TO 0.6 PPM TOTAL CHLORINE
‡ NO LIMITS AVAILABLE

to its corresponding azoxy compound (general form: ArN(O)=NAr) (13).

Summary of Results

Table 7 provides a summary of observations which compares the three dechlorinating agents when excess amounts of each are used.

TABLE 7

SUMMARY OF OBSERVATIONS

CONSEQUENCES OF ADDITION OF EXCESS DECHLORINATING AGENT

DECHLORINATION AGENT	CONTINUOUS EXTRACTION		SEPARATORY FUNNEL EXTRACTION
	Base/Neutral, Acid Extraction	Acid/Neutral, Base Extraction	Base/Neutral, Acid Extraction
SODIUM THIOSULFATE	Sulfur crystal formation. Acceptable but reduced recoveries for matrix spikes & surrogates. Low di-n-butyl phthalate recovery.	Sulfur crystal formation. Acceptable but generally reduced recoveries for matrix spikes & surrogates when compared to sodium arsenite & L-ascorbic acid.	Sulfur crystal formation. (No recovery data available).
SODIUM ARSENITE	Acceptable recoveries for all matrix spike and surrogate compounds. Low di-n-butyl phthalate recovery. No interference peaks.	Acceptable recoveries for all matrix spike and surrogate compounds. No interference peaks.	One small peak observed, but did not interfere. (No recovery data available).
L-ASCORBIC ACID	Acceptable recoveries for all cmpds. Low recoveries for 2,4-dinitrotoluene & di-n-butyl phthalate. Five interference peaks observed.	Good recoveries for all matrix spike and surrogate compounds. Two interference peaks observed.	No interference peaks observed. (No recovery data available).
EFFECTS OF CHLORINATION (NO DECHLORINATION)	Low recoveries of d_5-phenol; phenol; 4-chloro-3-methylphenol & di-n-butyl phthalate. Chlorination products formed.	Low recoveries of d_5-phenol; 4-chloro-3-methyl phenol; acenaphthene pyrene and phenol. Chlorination products formed.	Not analyzed. (No recovery data available).

Further Study of Sodium Thiosulfate

Method 625 recommends that 80 mg sodium thiosulfate per liter of sample be used as a dechlorinating agent. This amount presented a chromatographic problem when continuous extraction was performed (using either extraction sequence). Figure 6 showed the large molecular sulfur peak that eluted over a broad range (over 300 scans) and had a peak maximum at scan 1865. In contrast, Figure 7 showed the result when 20 mg of sodium thiosulfate per liter of sample was used. There is no apparent molecular sulfur peak, but a very small amount of sulfur was detected (peak maximum at scan 1876, barely detectable on the chromatogram).

The method of extraction greatly affected the amount of molecular sulfur recovered. Figure 8 contrasted continuous extraction with separatory funnel extraction when 80 mg/L of sodium thiosulfate was used. The upper chromatogram showed the large molecular sulfur peak obtained when continuous extraction was employed. In contrast, the lower chromatogram (separatory funnel extraction) indicated that no detectable sulfur was extracted by this method. Both chromatograms represent base/neutral, acid extraction schemes. Similar results were obtained for acid/neutral, base extractions.

Matrix and surrogate spike recoveries were acceptable for all analyses performed. Excellent recoveries were obtained by the continuous extraction method using either 80 mg/L sodium thiosulfate (Tables 8 and 9) or 20 mg/L (Tables 10 and 11). The separatory funnel extraction method gave significantly lower recoveries for certain phenolic compounds: 2-fluorophenol; d_5-phenol; phenol and 4-nitrophenol (Tables 12 and 13). This is due to more efficient extraction of hydrophilic compounds when continuous extraction is employed (7). However, it did give a greater recovery for di-butyl-phthalate when the extraction was carried out under base/neutral, acid extraction conditions. This compound hydrolyzes to a greater degree under continuous extraction conditions (7). All raw data for surrogate and spike recoveries is shown in Tables 11A through 22A in the Appendix.

As previously noted, sodium thiosulfate reduces chlorine according to the following equation (9):

$$\underset{\frac{(158\ g)}{mole}}{Na_2S_2O_3} + H_2O + \underset{\frac{(71\ g)}{mole}}{Cl_2} = Na_2SO_4 + S + 2HCl$$

One mole of sodium thiosulfate reduces one mole of chlorine. Stoichiometrically, the amount of sodium thiosulfate required is about twice as much as chlorine. It was found in this study that 20 mg of sodium thiosulfate reduced 10.5 mg of chlorine. The use of 20 mg of sodium thiosulfate should be sufficient

Figure 6

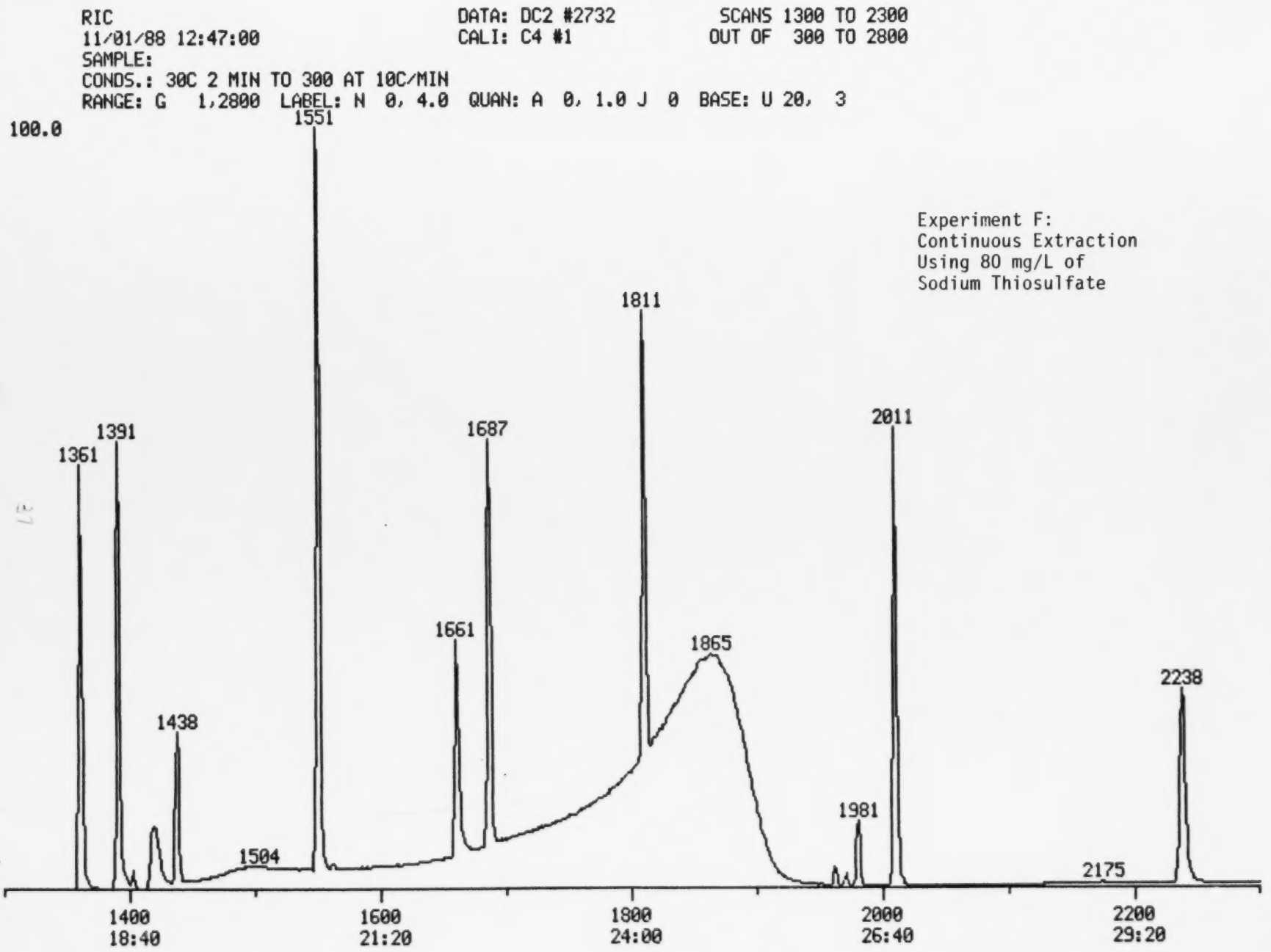

RIC
11/01/88 12:47:00
SAMPLE:
CONDS.: 30C 2 MIN TO 300 AT 10C/MIN
RANGE: G 1,2800 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: DC2 #2732
CALI: C4 #1
SCANS 1300 TO 2300
OUT OF 300 TO 2800
100.0
1551
1811
2011
1687
1391
1361
1661
1865
2238
1438
1981
1504
2175
Experiment F:
Continuous Extraction
Using 80 mg/L of
Sodium Thiosulfate
1400
18:40
1600
21:20
1800
24:00
2000
26:40
2200
29:20

Figure 7

RIC
10/17/88 10:03:00
SAMPLE: DECHLOR STUDY
CONDS.: 30C 2 MIN TO 300C AT 10/MIN
RANGE: G 1,2700 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

DATA: DC2 #2394
CALI: CAL12178 #2

SCANS 1500 TO 2500
OUT OF 500 TO 2700

Reproduced from best available copy.

Experiment F:
Continuous Extraction
Using 20 mg/L of
Sodium Thiosulfate

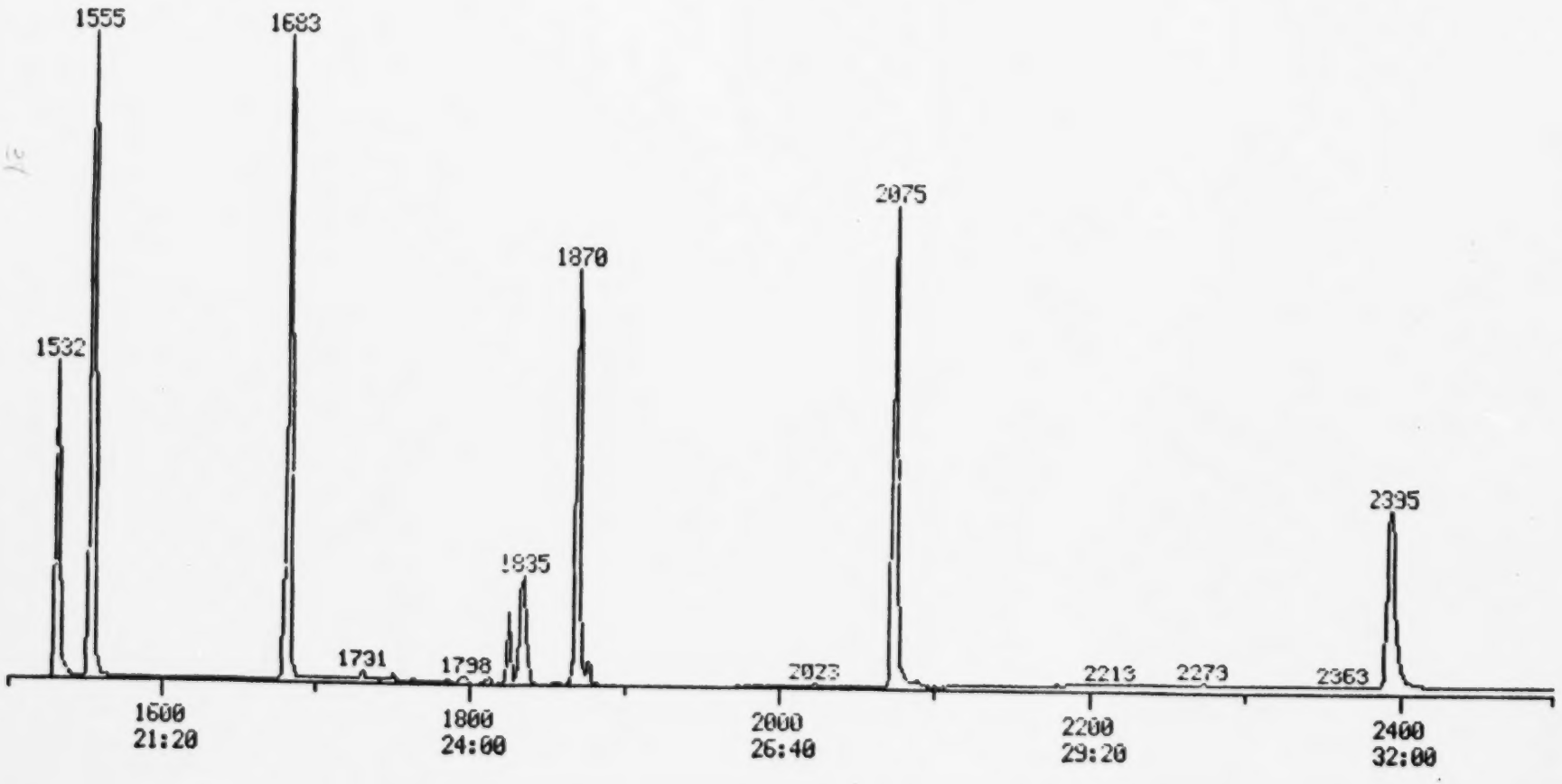


Figure 8

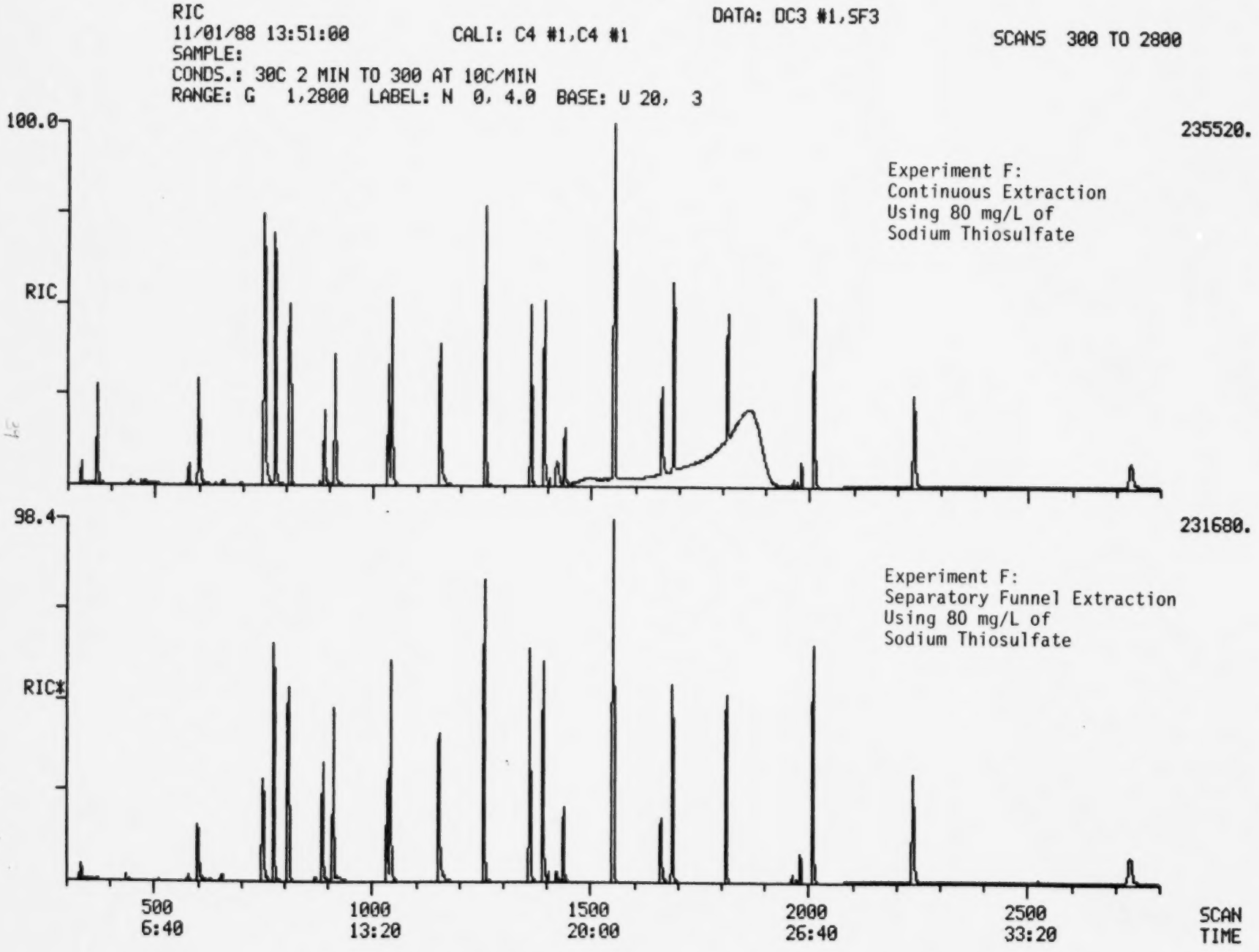

RIC
11/01/88 13:51:00
CALI: C4 #1,C4 #1
DATA: DC3 #1,SF3
SCANS 300 TO 2800
SAMPLE:
CONDS.: 30C 2 MIN TO 300 AT 10C/MIN
RANGE: G 1,2800 LABEL: N 0, 4.0 BASE: U 20, 3
100.0
235520.
RIC
Experiment F:
Continuous Extraction
Using 80 mg/L of
Sodium Thiosulfate
98.4
231680.
RIC
Experiment F:
Separatory Funnel Extraction
Using 80 mg/L of
Sodium Thiosulfate
500
6:40
1000
13:20
1500
20:00
2000
26:40
2500
33:20
SCAN
TIME

TABLE 8

EXPERIMENT F: CONTINUOUS EXTRACTION

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

SAMPLE EXTRACT

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
2-FLUOROPHENOL	87	81.7	21-100
D5-PHENOL	92.4	87.1	10-94
D5-NITROBENZENE	90.9	83.1	35-114
2-FLUORO-1,1'-BIPHENYL	88.8	82.7	43-116
2,4,6-TRIBROMOPHENOL	89	89.7	10-123
D14-P-TERPHENYL	89.7	84.4	33-141

EXTRACTS CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 9

EXPERIMENT F: CONTINUOUS EXTRACTION

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
PHENOL	93.1	85.1	12-89
2-CHLOROPHENOL	90.2	85.9	27-123
1,4-DICHLOROBENZENE	84.7	77.9	36-97
N-NITROSODI-N-PROPYLAMINE	106.9	90.9	41-116
1,2,4-TRICHLOROBENZENE	86.6	78.8	39-98
4-CHLORO-3-METHYLPHENOL	97.2	86.8	23-97
ACENAPHTHYLENE	86.3	80.3	46-118
4-NITROPHENOL	101.8	96.3	10-80
2,4-DINITROTOLUENE	94.2	83.5	24-96
PENTACHLOROPHENOL	112.2	110.9	9-103
DIBUTYLPHTHALATE	97.7	59.7	11-117
PYRENE	91.6	85.3	26-127

CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 10

EXPERIMENT F: CONTINUOUS EXTRACTION

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

SAMPLE EXTRACT

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
2-FLUOROPHENOL	94.3	80.7	21-100
D5-PHENOL	93.1	83.7	10-94
D5-NITROBENZENE	92.6	93.8	35-114
2-FLUORO-1,1'-BIPHENYL	98.2	91.1	43-116
2,4,6-TRIBROMOPHENOL	95.1	82.7	10-123
D14-P-TERPHENYL	93	91.5	33-141

EXTRACTS CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 11

EXPERIMENT F: CONTINUOUS EXTRACTION

MATRII SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
PHENOL	93.9	84.05	12-89
2-CHLOROPHENOL	95.6	83.1	27-123
1,4-DICHLOROBENZENE	90.75	85.15	36-97
N-NITROSODI-N-PROPYLAMINE	83.25	86.35	41-116
1,2,4-TRICHLOROBENZENE	98.4	89.55	39-98
4-CHLORO-3-METHYLPHENOL	91.8	89.45	23-97
ACENAPHTHYLENE	93.4	89.55	46-118
4-NITROPHENOL	84.6	82	10-80
2,4-DINITROTOLUENE	94.9	93.55	24-96
PENTACHLOROPHENOL	91.8	78.85	9-103
DIBUTYLPHTHALATE	92.95	65.25	11-117
PYRENE	89.95	90.85	26-127

CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 12

EIPERIMENT F: SEPARATORY FUNNEL EITRACTION

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

SAMPLE EITRACT

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
2-FLUOROPHENOL	55.3	50.2	21-100
D5-PHENOL	35.5	32.7	10-94
D5-NITROBENZENE	94.5	88.2	35-114
2-FLUORO-1,1'-BIPHENYL	89.3	76.9	43-116
2,4,6-TRIBROMOPHENOL	92.9	81.8	10-123
D14-P-TERPHENYL	95.3	92.1	33-141

EXTRACTS CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 13

EXPERIMENT F: SEPARATORY FUNNEL EXTRACTION

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	A/N (AVE)	B/N (AVE)	CLP LIMITS (WATER)
PHENOL	37.1	34.4	12-89
2-CHLOROPHENOL	88.9	80.3	27-123
1,4-DICHLOROBENZENE	65.8	61.4	36-97
N-NITROSODI-N-PROPYLAMINE	97.5	100.9	41-116
1,2,4-TRICHLOROBENZENE	69.3	63.8	39-98
4-CHLORO-3-METHYLPHENOL	92.6	82.5	23-97
ACENAPHTHYLENE	84.2	86.1	46-118
4-NITROPHENOL	18.6	14.6	10-80
2,4-DINITROTOLUENE	86.7	90	24-96
PENTACHLOROPHENOL	87.5	68.9	9-103
DIBUTYLPHTHALATE	90.1	80.2	11-117
PYRENE	87.4	89.9	26-127

CHLORINATED TO 1.6 PPM TOTAL CHLORINE

to neutralize the residual chlorine concentration of most effluents encountered in NPDES sampling.

Table 14 is a summary of the results obtained by further study of sodium thiosulfate.

TABLE 14

SUMMARY OF OBSERVATIONS

DECHLORINATION USING SODIUM THIOSULFATE

TYPE OF EXTRACTION	CONCENTRATION OF SODIUM THIOSULFATE 80 MG/L	20 MG/L
Continuous extraction (Acid/neutral, base).	Excellent recoveries for all matrix spikes & surrogates. Chromatographic interference of molecular sulfur.	Excellent recoveries for all matrix spikes & surrogates. No chromatographic interference due to molecular sulfur.
Continuous extraction (Base/neutral, acid).	Good but reduced recoveries for all matrix spikes & surrogates. Di-n-butyl phthalate recovery about 60%. Chromatographic interference of molecular sulfur.	Good but generally reduced recoveries for all matrix spikes & surrogates. Di-n-butyl phthalate recovery about 65%. No chromatographic interference due to molecular sulfur.
Separatory funnel extraction (Acid/neutral, base).	Generally good recoveries, except for some hydrophilic phenols which gave low recoveries. No chromatographic interference due to molecular sulfur.	Not analyzed. (No recovery data available).
Separatory funnel extraction (Base/neutral, acid).	Generally good recoveries, except for some hydrophilic phenols which gave low recoveries. No chromatographic interference due to molecular sulfur.	Not analyzed. (No recovery data available).

IX. CONCLUSION

The necessity to dechlorinate effluents was shown by results obtained from the chlorination of surrogate and matrix spikes. Phenolic concentrations decreased and various chlorophenols were produced. Under acid/neutral extraction conditions, chlorinated derivatives of acenaphthene and pyrene were also formed.

This study examined the suitability of three dechlorinating agents: sodium thiosulfate, L-ascorbic acid and sodium arsenite. Sodium thiosulfate, the compound required by Method 625 (1), gave good results when 20 mg per liter of sample was employed. Analytical and chromatographic problems were encountered when excess amounts (2.5-5.0 g) were used, mainly due to the molecular sulfur formed in the extraction process. These amounts were tested since the reagent is added in the field and it is conceivable that an excess could be added. The concentration of sodium thiosulfate stated in Method 625 (80 mg/L) produced a chromatographic interference of molecular sulfur when extracted by the continuous extraction method, though this level produced no problem when separatory funnel extraction was used. For this reason, 20 mg of sodium thiosulfate is recommended as an appropriate level for both types of extractions.

Sodium arsenite in excess gave acceptable recoveries of surrogate and matrix spike compounds, and presented no analytical problems. However, it is not recommended for field use due to its high toxicity. In addition, EPA approval as an alternate test procedure would be required for use of this compound in the analysis of NPDES samples (14).

The use of L-ascorbic acid has been recommended for dechlorinating samples for volatile analysis. Problems were encountered when excess amounts of this reagent were employed. L-ascorbic acid produced an interference peak that would interfere with the quantitation of bis(2-chloroisopropyl)ether. In addition, under base/neutral continuous extraction conditions, it greatly decreased the recovery of 2,4-dinitrotoluene. When 80 mg of L-ascorbic acid per liter of sample was used, good recoveries of 2,4-dinitrotoluene were obtained (base/neutral, acid extraction conditions). However, the unknown interference peak was observed in some, but not all, of the extracts. The extraction recovery of this unknown compound was highly variable when employing L-ascorbic acid, and thus the interference peak represents a possible source of contamination. For this reason, L-ascorbic acid is not recommended as a suitable dechlorinating agent.

The results of this work have illustrated the importance

of dechlorination of samples for semi-volatile organic analysis (EPA Method 625) (1). In addition, the importance of careful dechlorination is evident. Sampling personnel should be warned of the analytical problems associated with the addition of excess dechlorinating agent. It is recommended that sodium thiosulfate be carefully added to chlorinated samples in 20 mg/L increments, with mixing and verification of dechlorination using EPA method 330.4 (15) or 330.5 (16) between each addition.

X. REFERENCES

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XI. APPENDIX

Additional Analytical Data

TABLE 1A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
CHLORINATED EXTRACTS

COMPOUND	SAMPLE NUMBER 2	3	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	41.3	49.1	45.2	21-100
D5-PHENOL	8.1	8.8	8.45	10-94
D5-NITROBENZENE	73	80	76.5	35-114
2-FLUORO-1,1'-BIPHENYL	61.1	62.2	61.65	43-116
2,4,6-TRIBROMOPHENOL	67.6	78.3	72.95	10-123
D14-P-TERPHENYL	79.4	90.4	84.9	33-141

SAMPLES 2 AND 3: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 2A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING SODIUM THIOSULFATE

	SAMPLE NUMBER			CLP LIMITS
COMPOUND	4	5	AVERAGE	(WATER)
2-FLUOROPHENOL	58.7	44.7	51.7	21-100
D5-PHENOL	65.3	53.7	59.5	10-94
D5-NITROBENZENE	66.7	55.3	61	35-114
2-FLUORO-1,1'-BIPHENYL	56.4	50	53.2	43-116
2,4,6-TRIBROMOPHENOL	70.8	65.2	68	10-123
D14-P-TERPHENYL	72.4	66.3	69.35	33-141

SAMPLES 4 AND 5: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 3A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING SODIUM ARSENITE

COMPOUND	SAMPLE NUMBER 6	7	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	63.6	76.5	70.05	21-100
D5-PHENOL	72.2	81.9	77.05	10-94
D5-NITROBENZENE	74.9	85.2	80.05	35-114
2-FLUORO-1,1'-BIPHENYL	61.4	66.7	64.05	43-116
2,4,6-TRIBROMOPHENOL	86.2	84.3	85.25	10-123
D14-P-TERPHENYL	91.2	92.6	91.9	33-141

SAMPLES 6 AND 7: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 4A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

	SAMPLE NUMBER			
COMPOUND	8	9	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	81.3	79.4	80.35	21-100
D5-PHENOL	86	84.7	85.35	10-94
D5-NITROBENZENE	88.2	87.5	87.85	35-114
2-FLUORO-1,1'-BIPHENYL	73.9	74.5	74.2	43-116
2,4,6-TRIBROMOPHENOL	95.5	91	93.25	10-123
D14-P-TERPHENYL	95.5	98.6	97.05	33-141

SAMPLES 8 AND 9: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 4B

EXPERIMENT B: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

	SAMPLE NUMBER			
COMPOUND	10	11	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	85	74.5	79.75	21-100
D5-PHENOL	84.5	77.6	81.05	10-94
D5-NITROBENZENE	88.6	80.8	84.7	35-114
2-FLUORO-1,1'-BIPHENYL	73.7	71.3	72.5	43-116
2,4,6-TRIBROMOPHENOL	81.2	86.8	84	10-123
D14-P-TERPHENYL	82.6	90.3	86.45	33-141

SAMPLES 10 AND 11: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 5A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL,ACID)

MATRIX SPIKE RECOVERY
(REPORTED AS %)
CHLORINATED EXTRACTS

COMPOUND	SAMPLE NUMBER 2	3	AVERAGE	CLP LIMITS (WATER)
PHENOL	8.2	10.6	9.4	12-89
2-CHLOROPHENOL	100.8	110.6	105.7	27-123
1,4-DICHLOROBENZENE	72.6	78.6	75.6	36-97
N-NITROSODI-N-PROPYLAMINE	75	78.6	76.8	41-116
1,2,4-TRICHLOROBENZENE	78.6	83.6	81.1	39-98
4-CHLORO-3-METHYLPHENOL	32.1	35.2	33.65	23-97
ACENAPHTHYLENE	85.6	90	87.8	46-118
4-NITROPHENOL	66.8	66.7	66.75	10-80
2,4-DINITROTOLUENE	75.8	83.5	79.65	24-96
PENTACHLORDPHENOL	54	57.3	55.65	9-103
DIBUTYLPHTHALATE	30	39.4	34.7	11-117
PYRENE	79.6	85.7	82.65	26-127

SAMPLES 2 AND 3: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 6A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 4	5	AVERAGE	CLP LIMITS (WATER)
PHENOL	66.5	55.7	61.1	12-89
2-CHLOROPHENOL	67.6	57.5	62.55	27-123
1,4-DICHLOROBENZENE	70.2	57.7	63.95	36-97
N-NITROSODI-N-PROPYLAMINE	71.9	60.8	66.35	41-116
1,2,4-TRICHLOROBENZENE	71.7	60.8	66.25	39-98
4-CHLORO-3-METHYLPHENOL	73.7	62.6	68.15	23-97
ACENAPHTHYLENE	76.3	69	72.65	46-118
4-NITROPHENOL	82.3	58.1	70.2	10-80
2,4-DINITROTOLUENE	75.5	67.3	71.4	24-96
PENTACHLOROPHENOL	72.8	56.5	64.65	9-103
DIBUTYLPHTHALATE	35.4	26.5	30.95	11-117
PYRENE	73.3	65.9	69.6	26-127

SAMPLES 4 AND 5: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 7A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING SODIUM ARSENITE

COMPOUND	SAMPLE NUMBER 6	7	AVERAGE	CLP LIMITS (WATER)
PHENOL	77.1	82.9	80	12-89
2-CHLOROPHENOL	78.3	81.6	79.95	27-123
1,4-DICHLOROBENZENE	81.7	86.4	84.05	36-97
N-NITROSODI-N-PROPYLAMINE	80.8	90.8	85.8	41-116
1,2,4-TRICHLOROBENZENE	82.6	85.7	84.15	39-98
4-CHLORO-3-METHYLPHENOL	86.4	85	85.7	23-97
ACENAPHTHYLENE	92.8	90.2	91.5	46-118
4-NITROPHENOL	88.8	81.3	85.05	10-80
2,4-DINITROTOLUENE	89	91.6	90.3	24-96
PENTACHLOROPHENOL	75.1	86.6	80.85	9-103
DIBUTYLPHTHALATE	45.1	56.2	50.65	11-117
PYRENE	89.3	93.4	91.35	26-127

SAMPLES 6 AND 7: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 8A

EXPERIMENT A: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

COMPOUND	SAMPLE NUMBER 8	9	AVERAGE	CLP LIMITS (WATER)
PHENOL	89.7	86.1	87.9	12-89
2-CHLOROPHENOL	82	77.7	79.85	27-123
1,4-DICHLOROBENZENE	89	87.4	88.2	36-97
N-NITROSODI-N-PROPYLAMINE	92.1	91	91.55	41-116
1,2,4-TRICHLOROBENZENE	86.4	86.3	86.35	39-98
4-CHLORO-3-METHYLPHENOL	92.7	91.6	92.15	23-97
ACENAPHTHYLENE	90.2	89.6	89.9	46-118
4-NITROPHENOL	100.1	94.4	97.25	10-80
2,4-DINITROTOLUENE	60.4	61.1	60.75	24-96
PENTACHLOROPHENOL	108.9	104.1	106.5	9-103
DIBUTYLPHTHALATE	55.3	60.6	57.95	11-117
PYRENE	93	97.1	95.05	26-127

SAMPLES 8 AND 9: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 8B

EXPERIMENT B: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

COMPOUND	SAMPLE NUMBER 10	11	AVERAGE	CLP LIMITS (WATER)
PHENOL	90.7	82.2	86.45	12-89
2-CHLOROPHENOL	90.5	81.7	86.1	27-123
1,4-DICHLOROBENZENE	90.9	82.5	86.7	36-97
N-NITROSODI-N-PROPYLAMINE	93.7	86.9	90.3	41-116
1,2,4-TRICHLOROBENZENE	90.8	83.1	86.95	39-98
4-CHLORO-3-METHYLPHENOL	91.7	85.4	88.55	23-97
ACENAPHTHYLENE	92.1	86	89.05	46-118
4-NITROPHENOL	85.3	92.4	88.85	10-80
2,4-DINITROTOLUENE	90	91.9	90.95	24-96
PENTACHLOROPHENOL	88	101	94.5	9-103
DIBUTYLPHTHALATE	91.6	92.4	92	11-117
PYRENE	89.2	95.3	92.25	26-127

SAMPLES 10 AND 11: CHLORINATED TO 0.7 PPM TOTAL CHLORINE

TABLE 9A

EXPERIMENT D: CONTINUOUS EXTRACTION

AROMATIC NITRO COMPOUND RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

EXTRACTS

COMPOUND	BASE/NEUTRAL 1	BASE/NEUTRAL 2	ACID/NEUTRAL 1	ACID/NEUTRAL 2	CLP LIMITS (WATER)
2,4-DINITROTOLUENE	30.2	29.9	98.6	94.8	24-96
NITROBENZENE	94.5	102.4	105.9	105.5	NA[1]

B/N AND A/N EXTRACTS WERE CHLORINATED TO 0.9 PPM TOTAL CHLORINE
[1] NO LIMITS AVAILABLE

TABLE 10A

EXPERIMENT E: CONTINUOUS EXTRACTION
BASE/NEUTRAL, ACID EXTRACTION

DINITROTOLUENE RECOVERY
(REPORTED AS %)
DECHLORINATION USING L-ASCORBIC ACID

EXTRACTS

COMPOUND	BASE/NEUTRAL 1	BASE/NEUTRAL 2	BASE/NEUTRAL 3	BASE/NEUTRAL 4	CLP LIMITS (WATER)
2,4-DINITROTOLUENE	87.8	90.2	91.1	98.2	24-96
2,6-DINITROTOLUENE	90.4	93.6	86.4	90.0	NA‡

ALL SAMPLES WERE CHLORINATED TO 0.6 PPM TOTAL CHLORINE
‡ NO LIMITS AVAILABLE

TABLE 11A

EXPERIMENT F: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

	SAMPLE NUMBER			CLP LIMITS
COMPOUND	1	2	AVERAGE	(WATER)
2-FLUOROPHENOL	93.2	80.8	87	21-100
D5-PHENOL	95.8	88.9	92.35	10-94
D5-NITROBENZENE	95.7	86.1	90.9	35-114
2-FLUORO-1,1'-BIPHENYL	92.4	85.2	88.8	43-116
2,4,6-TRIBROMOPHENOL	90.5	87.5	89	10-123
D14-P-TERPHENYL	89.2	90.2	89.7	33-141

SAMPLES 1 AND 2: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 12A

EXPERIMENT F: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 3	4	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	81.5	81.8	81.65	21-100
D5-PHENOL	87.7	86.5	87.1	10-94
D5-NITROBENZENE	81.2	85	83.1	35-114
2-FLUORO-1,1'-BIPHENYL	82	83.4	82.7	43-116
2,4,6-TRIBROMOPHENOL	90.3	89.1	89.7	10-123
D14-P-TERPHENYL	83.2	85.6	84.4	33-141

SAMPLES 3 AND 4: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 13A

EXPERIMENT F: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)
MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 1	2	AVERAGE	CLP LIMITS (WATER)
PHENOL	92.5	93.7	93.1	12-89
2-CHLOROPHENOL	91.5	88.8	90.15	27-123
1,4-DICHLOROBENZENE	87.6	81.8	84.7	36-97
N-NITROSODI-N-PROPYLAMINE	111.4	102.4	106.9	41-116
1,2,4-TRICHLOROBENZENE	89.3	83.8	86.55	39-98
4-CHLORO-3-METHYLPHENOL	96.5	97.9	97.2	23-97
ACENAPHTHYLENE	87.9	84.7	86.3	46-118
4-NITROPHENOL	100.2	103.3	101.75	10-80
2,4-DINITROTOLUENE	97	91.4	94.2	24-96
PENTACHLOROPHENOL	107.5	116.9	112.2	9-103
DIBUTYLPHTHALATE	97.4	97.9	97.65	11-117
PYRENE	90.3	92.9	91.6	26-127

SAMPLES 1 AND 2: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 14A

EXPERIMENT F: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)
MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 3	SAMPLE NUMBER 4	AVERAGE	CLP LIMITS (WATER)
PHENOL	86.8	83.4	85.1	12-89
2-CHLOROPHENOL	87.5	84.2	85.85	27-123
1,4-DICHLOROBENZENE	77.1	78.7	77.9	36-97
N-NITROSODI-N-PROPYLAMINE	87.7	94.1	90.9	41-116
1,2,4-TRICHLOROBENZENE	77.7	79.9	78.8	39-98
4-CHLORO-3-METHYLPHENOL	84.1	89.5	86.8	23-97
ACENAPHTHYLENE	79.4	81.2	80.3	46-118
4-NITROPHENOL	91.4	101.1	96.25	10-80
2,4-DINITROTOLUENE	79.3	87.7	83.5	24-96
PENTACHLOROPHENOL	108.3	113.4	110.85	9-103
DIBUTYLPHTHALATE	56.8	62.6	59.7	11-117
PYRENE	83.3	87.3	85.3	26-127

SAMPLES 3 AND 4: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 15A

EXPERIMENT F: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

	SAMPLE NUMBER			
COMPOUND	1	2	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	98.6	90	94.3	21-100
D5-PHENOL	94.8	91.4	93.1	10-94
D5-NITROBENZENE	91.3	93.9	92.6	35-114
2-FLUORO-1,1'-BIPHENYL	103.6	92.7	98.15	43-116
2,4,6-TRIBROMOPHENOL	96.8	93.3	95.05	10-123
D14-P-TERPHENYL	96.2	89.8	93	33-141

SAMPLES 1 AND 2: CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 16A

EXPERIMENT F: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

	SAMPLE NUMBER			
COMPOUND	3	4	AVERAGE	CLP LIMITS (WATER)
2-FLUOROPHENOL	81.5	79.9	80.7	21-100
D5-PHENOL	85.7	81.7	83.7	10-94
D5-NITROBENZENE	96.7	90.9	93.8	35-114
2-FLUORO-1,1'-BIPHENYL	93.2	88.9	91.05	43-116
2,4,6-TRIBROMOPHENOL	82.2	83.1	82.65	10-123
D14-P-TERPHENYL	92.3	90.7	91.5	33-141

SAMPLES 3 AND 4: CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 17A

EXPERIMENT F: CONTINUOUS EXTRACTION (ACID/NEUTRAL, BASE)
MATRII SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 1	SAMPLE NUMBER 2	AVERAGE	CLP LIMITS (WATER)
PHENOL	95.9	91.9	93.9	12-89
2-CHLOROPHENOL	100.2	91	95.6	27-123
1,4-DICHLOROBENZENE	95.5	86	90.75	36-97
N-NITROSODI-N-PROPYLAMINE	80.2	86.3	83.25	41-116
1,2,4-TRICHLOROBENZENE	105.3	91.5	98.4	39-98
4-CHLORO-3-METHYLPHENOL	90.4	93.2	91.8	23-97
ACENAPHTHYLENE	96.1	90.7	93.4	46-118
4-NITROPHENOL	71.7	97.5	84.6	10-80
2,4-DINITROTOLUENE	95	94.8	94.9	24-96
PENTACHLOROPHENOL	88.1	95.5	91.8	9-103
DIBUTYLPHTHALATE	94.4	91.5	92.95	11-117
PYRENE	90.2	89.7	89.95	26-127

SAMPLES 1 AND 2: CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 18A

EXPERIMENT F: CONTINUOUS EXTRACTION (BASE/NEUTRAL, ACID)
MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 20 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 3	4	AVERAGE	CLP LIMITS (WATER)
PHENOL	85.5	82.6	84.05	12-89
2-CHLOROPHENOL	83.8	82.4	83.1	27-123
1,4-DICHLOROBENZENE	87.3	83	85.15	36-97
N-NITROSODI-N-PROPYLAMINE	90.2	82.5	86.35	41-116
1,2,4-TRICHLOROBENZENE	90.4	88.7	89.55	39-98
4-CHLORO-3-METHYLPHENOL	90.7	88.2	89.45	23-97
ACENAPHTHYLENE	90.3	88.8	89.55	46-118
4-NITROPHENOL	81.7	82.3	82	10-80
2,4-DINITROTOLUENE	94.4	92.7	93.55	24-96
PENTACHLOROPHENOL	78.1	79.6	78.85	9-103
DIBUTYLPHTHALATE	65	65.5	65.25	11-117
PYRENE	91.3	90.4	90.85	26-127

SAMPLES 1 AND 2: CHLORINATED TO 1.8 PPM TOTAL CHLORINE

TABLE 19A

EXPERIMENT F: SEPARATORY FUNNEL EXTRACTION (ACID/NEUTRAL, BASE)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

	SAMPLE NUMBER			
COMPOUND	1	2	AVERAGE	CLP LIMITS (WATER)
2-FLUORDPHENOL	50.4	60.1	55.25	21-100
D5-PHENOL	33.9	37	35.45	10-94
D5-NITROBENZENE	94.8	94.1	94.45	35-114
2-FLUORO-1,1'-BIPHENYL	88.1	90.5	89.3	43-116
2,4,6-TRIBROMOPHENOL	95.1	90.6	92.85	10-123
D14-P-TERPHENYL	95.9	94.6	95.25	33-141

SAMPLES 1 AND 2: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 20A

EIPERIMENT F: SEPARATORY FUNNEL EITRACTION (BASE/NEUTRAL, ACID)

SURROGATE SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

	SAMPLE NUMBER			CLP LIMITS
COMPOUND	3	4	AVERAGE	(WATER)
2-FLUOROPHENOL	49.5	50.8	50.15	21-100
D5-PHENOL	34	31.4	32.7	10-94
D5-NITROBENZENE	91.1	85.2	88.15	35-114
2-FLUORO-1,1'-BIPHENYL	77	76.8	76.9	43-116
2,4,6-TRIBROMOPHENOL	84.2	79.4	81.8	10-123
D14-P-TERPHENYL	93.8	90.3	92.05	33-141

SAMPLES 3 AND 4: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 21A

EXPERIMENT F: SEPARATORY FUNNEL EXTRACTION (ACID/NEUTRAL, BASE)
MATRIX SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER 1	SAMPLE NUMBER 2	AVERAGE	CLP LIMITS (WATER)
PHENOL	34.4	39.8	37.1	12-89
2-CHLOROPHENOL	87.3	90.5	88.9	27-123
1,4-DICHLOROBENZENE	59.5	72	65.75	36-97
N-NITROSODI-N-PROPYLAMINE	101.5	93.4	97.45	41-116
1,2,4-TRICHLOROBENZENE	62.8	75.8	69.3	39-98
4-CHLORO-3-METHYLPHENOL	93.2	92	92.6	23-97
ACENAPHTHYLENE	80.3	88.1	84.2	46-118
4-NITROPHENOL	26.2	10.9	18.55	10-80
2,4-DINITROTOLUENE	83.5	89.8	86.65	24-96
PENTACHLOROPHENOL	99.6	75.3	87.45	9-103
DIBUTYLPHTHALATE	86.4	93.8	90.1	11-117
PYRENE	83.5	91.2	87.35	26-127

SAMPLES 1 AND 2: CHLORINATED TO 1.6 PPM TOTAL CHLORINE

TABLE 22A

EXPERIMENT F: SEPARATORY FUNNEL EITRACTION (BASE/NEUTRAL, ACID)

MATRII SPIKE RECOVERY
(REPORTED AS %)
DECHLORINATION USING 80 MG/L SODIUM THIOSULFATE

COMPOUND	SAMPLE NUMBER		AVERAGE	CLP LIMITS (WATER)
	3	4		
PHENOL	34.5	34.3	34.4	12-89
2-CHLOROPHENOL	80.6	80	80.3	27-123
1,4-DICHLOROBENZENE	60.7	62	61.35	36-97
N-NITROSODI-N-PROPYLAMINE	115.1	86.7	100.9	41-116
1,2,4-TRICHLOROBENZENE	64	63.5	63.75	39-98
4-CHLORO-3-METHYLPHENOL	84.3	80.6	82.45	23-97
ACENAPHTHYLENE	90.6	81.6	86.1	46-118
4-NITROPHENOL	25.7	3.5	14.6	10-80
2,4-DINITROTOLUENE	96.7	83.3	90	24-96
PENTACHLOROPHENOL	84.8	53	68.9	9-103
DIBUTYLPHTHALATE	85.8	74.5	80.15	11-117
PYRENE	94.4	85.3	89.85	26-127

SAMPLES 3 AND 4: CHLORINATED TO 1.6 PPM TOTAL CHLORINE.